THE
VOLATILE OILS

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BY

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SECOND EDITION
BY
E. GILDEMEISTER.

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SCHIMMEL & CO., MILTITZ NEAR LEIPZIG.

Authorized translation by
EDWARD KREMERS
MADISON, WIS.

THIRD VOLUME.

WITH FIVE MAPS, ONE TABLE, AND NUMEROUS ILLUSTRATIONS.

LIST OF
ILLUSTRATIONS, MAPS, AND TABLES.

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ILLUSTRATIONS.

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Family: Lythraceæ.

Family: Myrtaceæ.

OILS OF UNKNOWN BOTANICAL ORIGIN.

SUPPLEMENT.

The Oils of the Agrumens.

The term agrumens, Ital. *Agrumi*, is applied to cultivated species of the genus *citrus*, the fruits of which, *e. g.* lemons, bitter and sweet oranges, limes, &c., are universally liked. These species do best in subtropic cultural zones, less well in the tropics where the fruits do not fully develop their aroma. They are cultivated on a large scale along the coast and in the islands of the Mediterranean. Italy is the leading country, the principal areas of production being Sicily and the neighboring Calabria. Other countries that should be mentioned are Spain, Portugal, southern France, the Azores, Morocco, Syria, and Malta. In California and Florida, large areas are devoted to the cultivation of lemon and orange trees. The West Indies supply limes. In South America, Australia, India, likewise in Japan and China the cultivation of citrus species is widely distributed. However, of all of these areas, distributed over the several continents, the very valuable agrumen oils are produced only in isolated districts. Thus the expressed oils, *viz.*, lemon, orange and bergamot oils, are produced in Sicily and Calabria; lime oil and orange oil in the West Indies. Southern France supplies neroli and petitgrain oils, Paraguay the latter only. In California a beginning has been made to obtain by extraction the oil of the fruits.

Whereas the oils from the leaves and flowers of the agrumens, such as neroli oil and petit grain oil, are obtained in the ordinary manner by distillation with water vapor, the oil from the fruits is produced by expression of the rinds for the reason that distillation yields a very inferior or even valueless product. The oil is contained in special cells in the outer layer of the rind. When ruptured these yield their odoriferous product.

In southern Italy, *i. e.* in Sicily and the southern point of Calabria, three different methods are in vogue for the production

of lemon, orange and bergamot oils: the *spugna* process, the *scorzetta* process and that involving the use of the *macchina*. The first two are described under oil of lemon, the third under oil of bergamot.

The *écuelle à piquer* is an instrument formerly used in Nice. It consists of a cup provided with erect brass needles and ending at the bottom in a tube. The fruits pricked by the needles yield the oil which collects in the tube and which, from time to time, is emptied into a larger receptacle. However, no rind oil is any longer produced in southern France, but the *écuelle* method is still used in the West Indies in the production of oil of lime. The extraction method practiced in California and already alluded to is applied to lemons and oranges.

At times, the immature fruits, also the expressed rinds and the slimy filter residues are distilled with water. The oil thus obtained is invariably of a very inferior quality and is used for adulteration of the poorest qualities of expressed oils.

The expressed agrumen oils are also designated "essences" in commerce.

Production and commerce. Unfortunately, no recent statistics are available as to the enormous production of bergamot, lemon, mandarine and orange fruits in southern Italy and the oils obtained therefrom. Hence reference must be made to the figures on p. 463 of the first edition of this text-book.

As to the exports of agrumen oils, statistics have been reported regularly in the Semi-Annual Reports of Schimmel & Co. These are from the pen of Mr. Ed. Jacob, Imperial Consul in Messina. They supply the amounts and values of oil exports for each of the four ports, *viz.,* Messina, Catania, Reggio and Palermo, also give the names of the countries to which the oils have been exported. In the following tables the more important data for the last few years are given.

Total exports 1890 to 1913.

1913	. . . .	731 712 kg.	valued at	21 686 005	lire
1912	. . .	829 343	„	„	20 405 277	„
1911	. . . .	767 371 „	„	„	15 679 825	„
1910	. . . .	629 897	„	„	„	11 970 810	„
1909	. . . .	604 299	„	„	„	11 676 575	„

1908 . . . 1 059 311	kg.	valued	at	21 138 675 lire
1907 . . . 1 056 899	„	„	„	24 173 030 „
1906 . . 948 328	„	„	„	18 556 053 „
1905 . . 868 244	„	„	„	13 709 760 „
1904 . . . 1 006 103	„	„	„	14 758 590 „
1903 . 864 770	„	„	„	11 964 839 „
1902 . 1 085 497	„	„	„	15 196 958 „
1898 . 667 293	„	„	„	9 015 083 „
1894 . . . 666 740	„	,	„	8 308 148 „
1890 . 301 879	„	.	„	5 056 214 „

Total exports 1912 and 1913.

1912

Messina .	617 693 kg.	valued	at	14 824 632 lire
Catania . .	90 555 „	„	„	2 173 320 „
Reggio . .	65 695 „	„	„	2 299 325 „
Palermo . .	55 400 „	„	„	1 108 000 „
Total	829 343 kg.	valued	at	20 405 277 lire

1913

Messina .	550 038 kg.	valued	at	16 501 140 lire
Catania .	33 993 „	„	„	1 019 790 „
Reggio . . .	47 305 „	„	„	1 655 675 „
Palermo . .	100 376 „	„	„	2 509 400 „
Total	731 712 kg.	valued	at	21 686 005 lire

Exports from the Italian ports to the principal countries of consumption in the year 1913.

United States of America.

Messina . . .	297 061 kg.	valued	at	8 911 830 lire
Catania . . .	9 853 „	„	„	295 590 „
Reggio . . .	5 109 „	„	„	178 815 „
Palermo . . .	33 740 „	„	„	843 500 „
Total	345 763 kg.	valued	at	10 229 735 lire

Great Britain.

Messina	112 029 kg.	valued	at	3 360 870 lire
Catania	4 583 „	„	„	137 490 „
Reggio . . .	307 „	„	„	10 745 „
Palermo	33 115 „	„	„	827 875 „
Total	150 034 kg.	valued	at	4 336 980 lire

1*

France.

Messina	40265 kg. valued at	1207950 lire
Catania	3600 „ „ „	108000 „
Reggio	24891 „ „ „	871185 „
Palermo	7396 „ „ „	184900 „

Total　76152 kg. valued at 2372035 lire

Austria-Hungary[1]).

Messina	44968 kg. valued at	1349040 lire
Catania	4437 „ „ „	133110 „
Reggio	1058 „ „ „	37030 „
Palermo . . .	18062 „ „ „	451550 „

Total　68525 kg. valued at 1970730 lire

North German Ports[1]).

Messina	10158 kg. valued at	304740 lire
Catania . . .	3477 „ „ „	104310 „
Reggio	12283 „ „ „	429905 „
Palermo	5606 „ „ „	140150 „

Total　31524 kg. valued at 979105 lire

Hence the percentage of the total export received by each country for the year 1913 is as follows: —

	p. c. amount	p. c value
United States	47,3	42,0
Great Britain	20,5	20,0
France	10,4	10,9
Austria-Hungary[1])	9,4	9,1
North German Ports[1])	4,3	4,3

From the foregoing figures the following average prices may be obtained. In 1913 the average price in Messina and Catania was 30 lire per kilo oil exported, in Reggio (mostly bergamot oil!) 35 lire, in Palermo 25 lire. In 1912 the respective values were for Messina and Catania 25 lire, for Palermo 20 lire and for Reggio 35 lire.

The finished oil, purified by filtration, enters commerce in copper flasks (Ger. *Ramieren*) of 25 to 50 kg. capacity (fig. 1).

As compared with the agrumen oil industry of southern Italy, which is restricted practically to Sicily and Calabria, the industry

[1]) In this connection it should be noted that most of the oil destined for Germany is shipped via Trieste, hence appears under Austria-Hungary in the statistics.

Fluctuations in the
price of
bergamot oil
and
lemon oil
for the years 1900 to 1914
as expressed
in marks per kilogram.

B   Bergamot oil
C   Lemon oil.

1003f

60 M

B

C

B

C
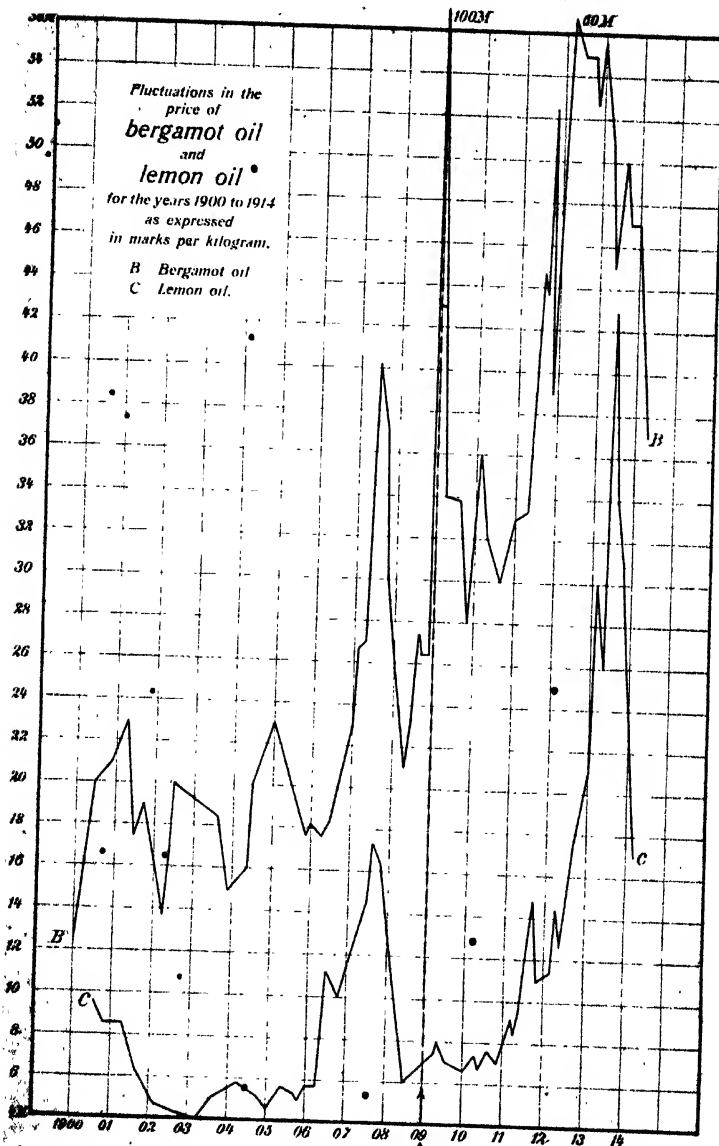
Earthquake in Messina.

of oils expressed elsewhere, with the exception of the lime oil produced in the West Indian island of Montserrat, scarcely comes into consideration. However, attempts have been made in North America in recent years to produce agrumen oils, particularly orange oil, namely in California, Florida and Jamaica. What extent these seemingly promising enterprises have assumed does not become apparent from available statistics. The quality of the oil produced corresponded in general to the customary standards.
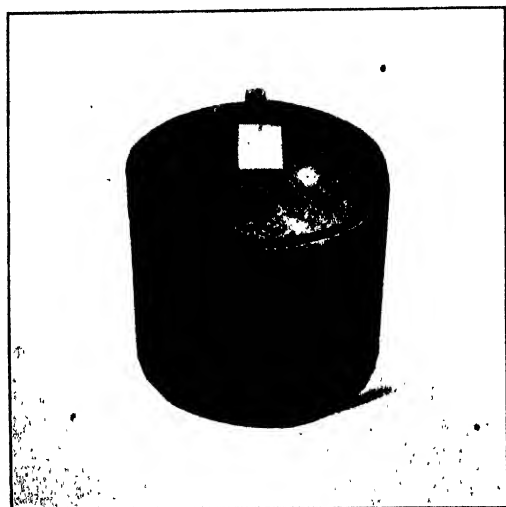
Fig. 1.

At the beginning of 1914 the amount of orange oil exported from Jamaica to the United States and Europe was not inconsiderable. The south Italian oil being high priced that from the new area of production could compete successfully.

The Italian production districts become apparent from the accompanying map, which was prepared in 1896 by a representative of the firm of Schimmel & Co. For the present edition it has been revised by Consul Ed. Jacob of Messina.

Bergamots are cultivated only in Calabria. The principal port of export for this oil is Reggio. Lemons and oranges are cultivated on the mainland as well as in Sicily.
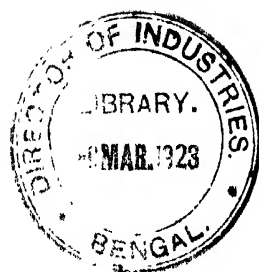
In Calabria lemon oil and bergamot oil are produced in the same localities. In Sicily the principal centers for the production of lemon oil are the provinces Messina, Catania, Siracusa and Palermo. The oils of the several districts not infrequently reveal fairly important deviations in their optical rotation. The angle of rotation of the Calabrian oils fluctuates between $+56°$ and $+62° 30'$.

In Sicily the principal production centers, when arranged according to the optical rotation of the oils, are as follows:

$a_{\scriptscriptstyle \rm D}$ = $+56$ to $+61$. Messina and vicinity, Nizza di Sicilia.

$a_{\scriptscriptstyle \rm D}$ $+59$ to $+63°$. Acireale, St. Teresa di Riva, Scaletta, St. Lucia, Patti, St. Agata, St. Stefano.

$a_{\scriptscriptstyle \rm D}$ $+61$ to $+64$. Catania, Giarre, Giardini, Acireale, Lentini, Vittoria, Comiso, Chiaramonte, Biscari.

$a_{\scriptscriptstyle \rm D}$ $+61$ to $+67$. Barcellona, Siracusa, Avola, Noto, Pachino.

Those localities in Palermo, colored yellow on the accompanying map, produce fruits but no oil, for the production of which the fruits are shipped to Palermo, to the vicinity of which the manufacture of the oil is restricted. The angle of rotation of the oils here produced varies between $+56$ and $+61°$; angles of rotation from $+61$ to $+63°$ are seldom observed.

417. Oil of Lemon.

Oleum Citri. — Citronenöl.   Essence de Citron.

Origin. On account of its fruits, the lemon tree, *Citrus medica*, L., subspec. *Limonum* (Risso), Hook. f. (*C. Limonum*, Risso; *C. medica* ,ß, L.), is cultivated principally in the countries bordering on Mediterranean Italy, Spain, Portugal, southern France, also in California and Florida. Up to the present time, the production of the oil, however, is carried on almost exclusively in Italy. Even here, aside from a small section of Calabria, it is restricted to Sicily. In this island, the tree thrives best on the mountain slopes toward the coast, more particularly in the valleys where irrigation of the lemon gardens, as the orchards are called, is possible (fig. 5 on p. 13). The distribution of the trees in Calabria and Sicily becomes apparent from the accompanying map.

. For the purpose of cultivation, young bitter orange trees raised from seed are grafted with twigs from the lemon tree. In the fifth year the tree begins to bear, producing about 200 fruits. A 15 to 20 years old tree yields 1000 fruits and a completely developed tree about 1700 to 2000 lemons[1]). Accord-• ing to other estimates, the latter yields as many as 3000 to 5000 lemons[2]).

Four harvest periods are differentiated. The principal harvest occurs in winter lasting from November to the beginning of April. As a rule only the winter fruits, the *Limoni* are used · for the production of oil. By withdrawing the water from the trees, the flowering period which naturally comes in April and May can be retarded. By irrigation at selected seasons flowering of the trees can be brought about. Thus three summer harvests can be brought about. The lemons of these harvests, however, are high priced and are not used in the production of oil. Those lemons which mature in April and May are known as *Bianchetti* because of their light color. Their oil has a low citral content and also a lower angle of rotation than the winter oil. The *Verdelli* are lemons with a greenish color that are harvested in June and July. The *Bastardoni* mature in August and the beginning of September.

Production. The principal Sicilian center of production of lemon oil is the *Etna district* ranging from Catania in the south to Giardini in the north. The second *district Messina*[3]) extends from Giardini to Messina. Then follows the *Palermo district,* which centers in the city of like name and which extends from Ficarazzi in the east to Partinico in the west. Next comes the

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[1]) A. S. Cheney, Lemon industry in Sicily. Americ. Perfumer 3 (1908), 160.

[2]) H. E. Burgess and J. F. Child, The lemon oil industry. Journ. Soc. chem. Industry 20 (1901), 1176.

[3]) The presentation which follows is based in part on several detailed and illustrated accounts. They are: U. S. Department of Agriculture, Bureau · of Plant Industry, Washington. Bulletin No. 160, October 6, 1909. Italian lemons and their by-products. G. H. Powell, The Italian lemon industry. E. M. Chace, The by-products of the lemon in Italy. -- E. M. Chace, The manufacture of flavoring extracts. Reprint from the Yearbook of Department of Agriculture for 1908, 337. -- Comp. also Report of Schimmel & Co. April 1896, 27.

Siracusa district in the southeast of the island. It extends from Avola in the south to Augusta in the north. Finally, the fifth or *Barcellona district* lies between Messina and Palermo. The small district in Calabria on the mainland is of interest only in so far as the oil there is produced by machinery.

The principal places of production in the several districts are:—

1. *Etna district.* Catania, Acireale, Giarre (not far from here is the village Carruba with the largest lemon oil factory in Sicily, in which several hundred pounds of oil are produced daily), Mascali, Fiumefreddo, Giardini.

2. *Messina district.* Santa Teresa, Roccalumera, Scaletta, Zanglea, Galati, Tremestieri, Mili, Contesse, Messina, perhaps also Bauso and Rometta.

3. *Palermo district.* Palermo, Monreale, Ficarazzi, Partinico, Carini and Cinisi.

4. *Siracusa district.* Avola, Siracusa, Floridia, Priolo, Augusta and Melilli.

5. *Barcellona district.* Barcellona, Patti and Santa Agata di Miletello.

The production of the oil usually lasts from December to the end of March and is rarely extended into the month of May. In Palermo, however, where the production begins later it lasts into the month of June. Around Siracusa the campaign begins earlier, about October 15, and lasts until April 15. All those lemons that will not stand transportation are used for the production of oil, which is obtained according to one of these methods:—

According to the first or *scorzetta* method the lemon rind is cut into halves; according to the second into thirds; and according to the third, the machine process, not at all.

The *scorzetta* method (fig. 6, p. 15) is employed in the Etna, Messina and Siracusa districts, also in Patti and St. Agata di Miletello. According to this method, the fruit is cut into halves by means of a special knife (fig. 2) either longitudinally or cross-wise; longitudinally if the rind is to be further used. The pulp is removed by means of a spoon-like tool (fig. 3). The hemispheres of the rind are moistened with water and set aside for from 4 to 5 hours or over night. This is said to facilitate the expression of the oil and to increase the yield (fig. 7, p. 19).

Whereas these preliminary operations are mostly conducted
by women and children, the expression is carried out by men.
(Fig. 8, p. 21 and fig. 9, p. 23.)   The periods of labor last from
2 o'clock in the morning until noon.   The men sit on low stools
with an earthenware jar before them (fig. 4).   This jar has a •
height of from 20 to 25 cm., a like diameter and is provided ₁
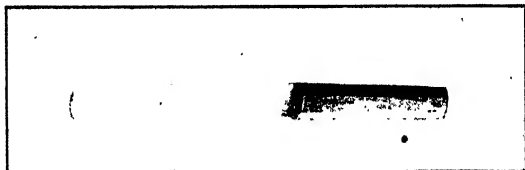
Fig. 2.

with a lip.   Just below the lip is a depression which serves to
retain the water and residues.   Across the middle of the jar
rests a bamboo stick 2 to 3 cm. in thickness.   This supports
three sponges: first a flat sponge, then a somewhat thicker one
and finally a cup shaped sponge.   Into the last the lemon rind
is pressed with the right hand whereas the left hand presses
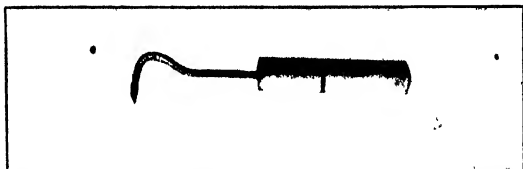
Fig. 3.

the sponge.   The rind is then turned somewhat and again
pressed.   This operation is repeated three or four times.   These
manipulations, however, are performed with such dexterity that
the expressed rinds seem to fly uninterruptedly into the basket
intended for their reception.   For the longitudinally cut rinds,
a large round sponge is used in place of the cup-shaped one.
After a sponge has served about 10 days it becomes valueless
because it acquires a tendency to get brittle and, therefore, has
lost the capacity to absorb the oil any longer.

The oil is decanted carefully from the water and the residues. The water and residues are further separated by means of a cloth strainer and from the residues of several days' operations, the last traces of oil are expressed by means of a hand press. This latter oil is known as *fece* and is of inferior quality and of less pleasant odor. It is not sold as such but mixed with the other oils. This method, according to which the fruits are halved as described, has the advantage that the hemispheric

Fig. 4.

rinds are not broken but retain their original shape. They can be pickled with salt and exported as *salato*. Moreover the pulp remains relatively intact and can be more advantageously used for the manufacture of citric acid, than is possible if the fruit is treated according to the *spugna* method. After having been expressed for both oil and juice, the fruit residues are useful only as fodder.

The *Processo alla spugna* is used side by side with the *scorzetta* method in Palermo and Barcellona. It differs from the method described principally in the preliminary operations of the lemon. Three longitudinal incisions are made and the

rind is removed from the fruit. On the one hand considerable
pulp adheres to the rind and on the other some rind remains
at the ends of the fruit. Hence a less complete separation of
rind and pulp is effected. For the expression of the rind no
cup-shaped sponge but a large round one is used, which lies
over the other two and against which the flattened rind is pressed.
Since some of the pulp adheres to the rind, it is natural that
the expressed liquid should contain more juice and residues
than that obtained by the previously described method. This
oil, however, has the advantage of filtering more readily and
remaining clear longer. This advantage is explained by assuming
that a number of substances dissolved in the oil, and which
otherwise separate later, are coagulated by the citric acid and
thus removed.

In Palermo and Barcellona the oil contained in the residues
is not expressed but recovered by a primitive method of water
distillation. The oil thus obtained is greatly inferior, has an
unpleasant odor and is colorless. It is admixed with the ex-
pressed oils.

Upon expression, 1000 lemons yield 320 to 640 g. of oil.
In other words 3100 to 1550 lemons are necessary for 1 kg. of
oil. Immature fruits are said to yield more oil than mature ones.

The use of a *machine*, described under bergamot oil on
p. 58, is restricted to Calabria. The amount of oil thus obtained
does not equal 5 p. c. of the total production. It has a more
decided color than the oils obtained according to the two other
methods. It is reported to be used principally for the adulteration
of bergamot oil or for giving a darker color to light oils.

Extraction method. Inasmuch as the high price of labor
prohibits the production of expressed agrumen oils in the United
States, a beginning was made about ten years ago to obtain the
oils by means of extraction with volatile solvents. They have
been designated "oleoresins" and differ from the expressed oils
by their darker color and by their higher content of non-volatile
extractive. To what extent they may replace expressed oils, the
future only can tell. The constants of these products are enu-
merated under "Properties".

Production by means of water distillation in vacuum. While
it is true that the production of agrumen oils by expression has the
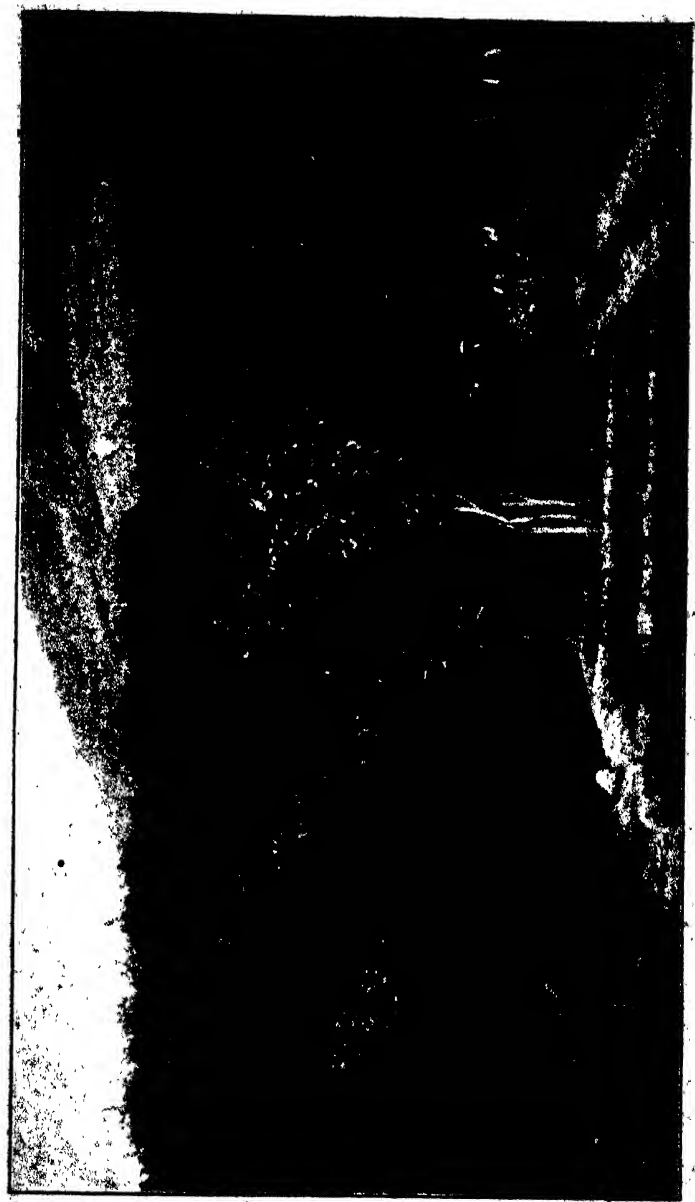
Fig. 5. Lemon grove in the Messina district.

advantage of not exposing the oils to higher temperatures so that
:he finished product contains the volatile constituents in the form
in which they are found in the plant, this method has disadvan-
tages not to be overlooked. First of all; it demands the much
more expensive human labor; and secondly, much of the oil
remains in the rind, hence is lost. Inasmuch as the common
method usually employed in the production of volatile oils, *viz.*
distillation with water vapor under atmospheric pressure, is not
applicable because malodorous and unstable products are obtained,
distillation in vacuum has been tried.

According to a new process, patented by Professors Pera-
toner and Scarlata, the lemons are cut and the comminuted
particles expressed so firmly that the juice carries with it the
oil liberated from the ruptured cells. The acid liquid thus ob-
tained is subjected to distillation under diminished pressure so
that the temperature never rises above 60´. The residue freed
from oil is utilized in the manufacture of citric acid.

In the Chemico-Pharmaceutical Institute of the University of
Palermo, Patanè and Carelli[1]) have compared the results obtained
according to this method with those obtained by the older pro-
cess of expression by hand. Parallel experiments yielded 0.12
and 0.136 p.c. for destillation, and 0.115 and 0.16 p.c. for expres-
sion by hand. Hence, so far as yield is concerned, both methods
yield results that differ but little.   •

Schimmel & Co.[2]) have retested the method and have ob-
tained appreciably higher results. They, however, proceeded
somewhat differently. The yellow layer containing the oil cells
was removed by peeling and the thin sections thus obtained were
comminuted by machinery as finely as possible. To the pulp
rich in oil considerable water was added, but not expressed.
The thin mixture was subjected to distillation under a pressure
of from 50 to 60 mm. until the distillate no longer separated any
oils drops. Indirect heating with jacket steam was avoided and
only steam passed directly into the mixture employed. The aque-
ous distillate was not cohobated but was utilized in thinning out
the magma of the next batch of comminuted rind.

[1]) Bollettino del Ministerio di Agricoltura, Industria è Commercio. Anno IX,
Serie C, fascicolo 9, p. 21.
[2]) Report of Schimmel & Co. April 1912, 70.

Fig. 6. Halving of the lemons (Palermo).

In this manner Schimmel & Co. obtained 0.3 p.c. of oil com
puted with reference to the original lemons. The oil had a pure
odor and revealed the following constants:

d_{15o} 0.8551; $\alpha_D + 55°30'$; α_D of the first 10 p.c. of distillate $+ 48°$;
citral 3.4 p.c.,

d_{15o} 0.8547; $\alpha_D + 56°22'$; α_D „ „ „ 10 p.c. „   „ $+ 50°40'$;
citral 4.5 p.c.

With the increase in temperature, the distillation proceeds
more favorably and a better yield is obtained, however, the aroma
of the oil suffers. With a reduced temperature the resulting oil
has a purer odor, but its volatilization diminishes, hence the
yield diminishes and, what is more, less of the difficultly volatile
citral passes over.

Preparation of concentrated, terpene-free lemon oil. The
production of concentrated lemon oils free from the but slightly
odorous terpenes is carried out in several ways, the factories
working according to methods that are kept secret. Some are
based on fractional distillation, with or without vacuum; others
on the greater solubility of the non-terpenes in dilute alcohol.
Still others are based on a combination of both principles. Hence
it is not surprising that the resulting products differ greatly. A
decided difference in the angle of rotation is observed if the
terpenes only are removed or both terpenes and sesquiterpenes.
In the former instance the concentrated oil is lævogyrate, in the
latter dextrogyrate.

Properties. Lemon oil is a light yellow liquid possessing
the agreeable odor of fresh lemons and an aromatic, mild and,
somewhat later, bitter taste. Inasmuch as oils produced in
geographically not distant districts reveal decided differences in
their properties (see the accompanying map), it is difficult to
establish limit values of general applicability. Moreover, the
season and degree of maturity of the fruit exert a marked influence
on the properties of the oils. Thus *e. g.* the oils expressed from
the fruits collected early in the campaign *i. e.* in November,
reveal the highest optical rotation, which diminishes with the
increasing maturity of the fruit as the winter advances. At the
same time specific gravity and citral content increase. Thus it
sometimes occurs that with a small crop of fruits a shortage of
oil results. In consequence thereof lemons are expressed which

in normal years are used for other purposes. Thus it happened
in 1913, when the price of lemon oil rose to the enormous height
of -// 43.— per 1 kg., that during the months of April and May
much oil was expressed from the socalled *bianchetti* lemons
(see p. 8), which revealed a low citral content and an angle of
rotation as low as, + 54 . It is further noteworthy that climatic
conditions, such as continued drought or cold weather, influence
the properties of the oil.

Generally speaking the *specific gravity* lies between 0.856 and
0.861, but 0.854 has been observed as lower limit in connection
with pure oils.

The *optical rotation*[1]), as a rule, fluctuates between +57 '
and +61 '. However, as becomes apparent from the accompanying
map, certain districts, more particularly in the western part of
the islan ', produce oils with an angle of rotation of but +56 '.
In one instance Chace[2]) observed as low as 54.16". In other
districts the angle of rotation rises to +67".

The *evaporation residue*, the determination of which is
discussed under bergamot oil, varies between 2.1 and 4 p.c.
However, in oils obtained by the machine process it is higher
and rises to 5[3]) and even 6.6 p.c.[4]). A.V. of the evaporation
residue 19 to 39; E.V. 100 to 214. However, the E.V., of small
amounts of evaporated oil (5 to 10 g.) does not drop below 150,
whereas that of the residue of larger amounts of oil has been
observed as low as 100. This apparently is due to the resini-
fication because of the longer period of evaporation.

The *index* of *refraction* n_{D20}. lies between 1.474 and 1.476.

[1]) Because of the reasons mentioned under orange oil (footnote 1 on
p. 53) it is necessary to determine the angle of rotation at 20° or to compute
it with reference to this temperature. If the determination is made at a
temperature below 20°, nine minutes should be deducted for every degree
below 20°; if made above 20 , 8.2 minutes should be added for every degree
in temperature.

[2]) The occurrence of pinene in lemon oil. U. S. Dept. of Agricult., Bur.
of Chemistry, Circular No. 46, p. 17.

[3]) E. Bertè and G. Romeo, *Annali del laboratorio chimico della camera
di commercio ed arti della provincia di Messina.* Messina 1908; Report of
Schimmel & Co. April 1909), 50.

[4]) Observations made in the laboratory of Schimmel & Co.

Solubility. Because of the mucilaginous and wax-like substances which accompany the citraptene (see under Composition, p. 28) the oil is mostly not perfectly soluble in (6 to 8 vol. of) 90 p. c. alcohol. However, it forms a clear solution with 0.5 to 1 vol. of 95 p. c. alcohol and with every proportion of absolute alcohol, ether, chloroform, benzene and amyl alcohol. Because of the slight water content of the oil, its solutions in carbon disulphide and benzin are mostly turbid[1]).

The citral content of lemon oil varies from 3.5 to 4 and even 5 p. c. when determined according to Kleber's method. (For details see p. 41 under Examination).

As to the optical rotation of the first 10 p. c. of fractionated distillate, see p. 43.

Properties of terpene-free lemon oil.

As pointed out on p. 16 the methods by which the terpene-free lemon oils[2]) are prepared by the several manufacturers differ greatly hence the products differ accordingly. It is, therefore, impossible to establish limit values. Moreover, a distinction is made between those deprived merely of their terpenes and those deprived of both terpenes and sesquiterpenes. In connection with a number of such concentrated oils, E. J. Parry[3]) has observed the following limit values:

	Terpene-free	Free of terpenes and sesquiterpenes
d_{15} . . .	0.8935 to 0.899	0.898 to 0.902
α_D . . .	$- 5^\circ$ to $- 8^\circ 30'$	$\cdot 1^\circ$ to $- 3^\circ 45'$
n_D . .	abt. 1.4810	—
Citral .	42 to 48 p. c.	An average of 65 p. c. or somewhat higher.

In connection with two terpene- and sesquiterpene-free oils made by himself, E. Bœcker[1]) observed the following constants: d_{15} 0.8951 and 0.8971; α_D 7° 10′ and - 5° 40′; the one oil required 1.4 vol. of 80 p. c. alcohol to form a clear solution, the other 0.9 vol.

[1]) Comp. vol. I, p. 566.

[2]) Comp. E. Bœcker, *Über terpen- und sesquiterpenfreie Öle.* Wallach Festschrift. Göttingen 1909, p. 201. — Journ. f. prakt. Chem. II. 81 (1910), 266 90 (1914), 393.

[3]) Chemist and Druggist 83 (1913), 378.

Fig. 7. Removal of the pulp from the lemons (Messina).

For the determination of the hydrocarbon and citral contents of concentrated oils see p. 48.

Properties of other special oils.

An authentic sample of oil prepared by the *machine process* had the following properties: color green; d_{15} 0.8630; $\alpha_{D20°} + 58°5'$; α_D of the first 10 p.c. $+ 56°34'$; n_{D20} 1.47695; evaporation residue 6.6 p.c. with an A.V. of 25.5 and an E.V. of 136.7; citral content 6 p.c.[1]).

The constants of a *Spanish* lemon oil were as follows: d_{15} 0.862; $\alpha_{D20} + 63°32'$; α_D of the first 10 p.c. $+ 67°10'$.

In connection with a *California* oil[2]) the following constants were found: d_{15} 0.8598; $\alpha_{D20} + 53°56'$; α_D of the first 10 p.c. $+ 48°42'$; n_{D20} 1.47490; evaporation residue 3.6 p.c.

The color of a *Concrete Oleoresin* of *Lemon* (comp. p. 12) was dark olive; d_{15} 0.8730 to 0.8836; $\alpha_{D20°} + 57°30'$ to $+ 60°30'$; α_D of the first 10 p.c. $+ 54°11'$ to $+ 69°40'$; evaporation residue 14.2 to 15.4 p.c.; A.V. of the evaporation residue 25.4; E.V. 102.1; citral content 6 p.c.

Properties of *lemon oil terpenes*: d_{15} 0.852 to 0.854; $\alpha_{D20} + 62$ to $+ 72$; n_{D20} 1.473 to 1.475; soluble in 6 to 7 vols. or more of 90 p.c. alcohol and in 1.7 vols. or more of 95 p.c. alcohol.

Storage. Like all volatile oils obtained by expression, lemon oil deposits a more or less crystalline sediment upon standing.

Both air and light cause rapid changes: the oil looses its color and a viscous, brown mass is deposited. At the same time the specific gravity as well as the solubility in 90 p.c. alcohol is increased. These changes correspond to those observed in connection with old turpentine oil that has been stored improperly. Hence, lemon oil should be kept in well filled, closely stoppered containers, stored away from light and in a cool place.

Composition. Although lemon oil has long been known, it required a relatively long time to acquire an even superficial insight into this complex mixture. The study of its numerous components was not rendered more easy by the presence of

[1]) Unless otherwise stated, the citral content has been determined by the Kleber method (see p. 41).

[2]) Réport of Schimmel & Co., October 1905, 28.

Fig. 8. Expression of the lemon oil from the rinds (Messina).

non-volatile constituents since their removal, even by steam distillation, could not be effected without practical decomposition of the volatile constituents.

A critical study of the extensive literature [1]), which cannot be taken up in detail, reveals the fact that some of the oils examined formerly were adulterated with turpentine oil. This is not surprising for it has only recently been demonstrated that lemon oil should contain at most, traces of pinene.

The early analyses of the oil revealed its low oxygen content. Individual chemists even went so far to declare it to be free from oxygen. This error resulted from the practice to use rectified oils for investigation, in the preparation of which the oxygenated constituents remained in the residue.

Arranged according to their boiling points, the following constituents have thus far been observed: --

1. *Octylene* (?). In connection with the study of the more volatile constituents of large quantities of lemon oil, H. E. Burgess and T. H. Page [2]) isolated a hydrocarbon possessing the following properties: d 0.7275; $\alpha_0 \pm 0°$; $n_{0.15}$ 1.4066; b. p. 123 to 124° (768 mm.); molecular refraction 38.54. Molecular weight determination and elementary analysis yielded values corresponding with the formula C_8H_{18} or C_8H_{16}. Inasmuch as the hydrocarbon yielded butyric acid upon oxidation with potassium permanganate, Burgess and Page concluded that it is octylene and regard it as a normal constituent of the oil.

2. *α-Pinene*. At times this terpene seems to be wanting entirely, at times it is present in such small amounts that its detection is coupled with difficulty. On account of the importance as to whether pinene is a natural constituent of lemon oil,

[1]) T. de Saussure, Anm. de Chim. et Phys. II. 13 (1820), 262; Liebig's Annalen 3 (1832), 165. -- Dumas, Ann. de Chim. et Phys. II. 52 (1833), 45; Liebig's Annalen 6 (1833), 255 and 9 (1834), 61. — Blanchet and Sell, Liebig's Annalen 6 (1833), 280. — E. Soubeiran and H. Capitaine, Journ. de Pharm. II. 26 (1840), 1; Liebig's Annalen 34 (1840), 317. — Gerhardt, Compt. rend. 17 (1843), 314. — Berthelot, Ann. de Chim. et Phys. III. 37 (1853), 233, 38 (1853), 44 and 40 (1854), 36. — Liebig's Annalen 88 (1853), 346. — A. Oppenheim, Berl. Berichte 5 (1872), 628. — J. Lafont, Bull. Soc. chim. II. 48 (1887), 777 and 49 (1888), 17; Chem. Zentralbl. 1888, I. 107.

[2]) Journ. chem. Soc. 85 (1904), 1328.

Fig. 9. Expression of lemon oil from the rinds (Palermo).

Schimmel & Co.[1]) in 1897 endeavored to isolate the hydro-
carbon by careful fractionation of 50 kg. of lemon oil in vacuum.
However, they obtained but 0.016 p. c. distilling below 170°.
Inasmuch as this fraction did not possess the properties of
pinene and since a second experiment yielded like results, the
chemists of this firm denied its presence. From a corresponding
lævogyrate fraction H. E. Burgess and J. F. Child[2]) later obtained
a hydrochloride addition product that melted at 124°, hence
concluded the presence of *l*-pinene. A further investigation of
the subject enabled Schimmel & Co.[3]) to identify a very insig-
nificant amount of pinene by means of its nitrol benzylamide.
Still later Schimmel & Co.[4]) examined 36 samples of lemon
oil obtained from reliable sources and found traces of pinene
in each.

From these investigations the conclusion may be drawn that
pinene frequently occurs in minimal amounts in normal lemon
oil, but that occasionally it is completely wanting. Under what
conditions the lemon tree produces pinene and under what
conditions it produces oil free from pinene, has not yet been
ascertained.

A method worked out by E. M. Chace for the detection of
minimal amounts of pinene in lemon oil is described in detail
on p. 44.

3. *Camphene.* Schimmel & Co.[5]) having expressed the opinion
that camphene might be contained in lemon oil, its presence was
demonstrated by Burgess and Child[6]) by the preparation of *iso*-
borneol from the corresponding fraction.

4. *β-Pinene.* From fraction 165 to 168 E. Gildemeister and
W. Müller[7]) obtained, upon oxidation, nopinic acid (m. p. 126°)
and nopinone (m. p. of semicarbazone 188°) thus proving the
presence of *β*-pinene in the oil.

[1]) Report of Schimmel & Co. April 1897, 19; October 1897, 22.
[2]) Journ. Soc. chem. Industry 20 (1901), 1176.
[3]) Report of Schimmel & Co. April 1902, 33; October 1902, 38
[4]) *Ibidem* October 1908, 50.
[5]) *Ibidem* October 1902, 39.
[6]) Chemist and Druggist 62 (1903), 476.
[7]) Wallach-Festschrift, Göttingen 1909, p. 441. -- Report of Schimmel & Co.
October 1909, 63.

5. *β-Phellandrene.* This was first detected by Schimmel & Co.[1]), and identified by its nitrite melting at 102 . This was verified by Gildemeister and Müller[2]) who, upon oxidation with dilute permanganate solution, obtained a liquid glycol which, when boiled with dilute hydrochloric acid, yielded a hydrocuminic aldehyde the semicarbazone of which melted at 203 to 204 . (Comp. vol. I, p. 326).

6. *Methylheptenone.* If the mixture of aldehydes and ketones, separated from the oil by means of bisulphite, be fractionated, methyl heptenone can be identified in fraction 174 to 179 by means of elementary analysis and the semicarbazone melting at 136 to 137 [3]).

7. *γ-Terpinene.* Upon oxidation of the hydrocarbons boiling above 173 , Gildemeister and Müller[4]) obtained the erythritol of γ-terpinene (m. p. 237), thereby proving for the first time the presence of this terpene in a volatile oil.

8. d-*Limonene.* This is quantitatively the principal constituent of the oil (m. p. of tetrabromide 104 to 105)[5]).

W. A. Tilden[6]) pointed out that the limonene from lemon oil is much less pure than that obtained from oil of orange. Upon oxidation of the limonene fraction, designated by him as citrene, he obtained paratoluic acid and terephthalic acid, two acids which do not result upon the oxidation of the corresponding fraction of orange oil. Citrene also behaves differently from limonene when treated with concentrated sulphuric acid. As with limonene resinification, due to the formation of polymeric products, results. In addition, however, cymene, $C_{10}H_{14}$, can be identified among the products readily volatile with water vapor. Naturally the presence of cymene after the application of so energetic a reagent as sulphuric acid cannot be regarded as proof of its presence in the original oil. It is more likely that the cymene resulted from the phellandrene or from the γ-terpinene discovered much later. As a matter of fact neither cymene

[1]) Report of Schimmel & Co. October 1897, 26.

[2]) *Loc. cit.* p. 441.

[3]) Report of Schimmel & Co. October 1902, 39.

[4]) *Loc. cit.* p. 443.

[5]) Wallach, Liebig's Annalen 227 (1885), 290.

[6]) Pharmaceutical Journ. III. 5 (1877), 190 and 9 (1879), 654.

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From these investigations the conclusion may be drawn that pinene frequently occurs in minimal amounts in normal lemon oil, but that occasionally it is completely wanting. Under what conditions the lemon tree produces pinene and under what conditions it produces oil free from pinene, has not yet been ascertained.

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[2]) Journ. Soc. chem. Industry 20 (1901), 1176.

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[5]) *Ibidem* October 1902, 39.

[6]) Chemist and Druggist 62 (1903), 476.

[7]) Wallach-Festschrift, Göttingen 1909, p. 441. — Report of Schimmel & Co. October 1909, 63.

11. *α-Terpineol* has been found in the higher boiling fractions which had been freed from aldehydes. It was identified by means of its phenylurethane melting at 110° [1]).

12. *Citral.* From the aroma point of view, *citral*, $C_{10}H_{16}O$, is the principal constituent of the oil. This aldehyde was discovered in the 'laboratory of Schimmel & Co. in 1888 by J. Bertram in oil of lemon [2]). The amount of this aldehyde varies between 3.5 and 5 p.c. (Kleber's method). For its assay see pp. 30 to 43.

13 and 14. *Linalyl and geranyl acetates.* According to J. C. Umney and R. S. Swinton [3]) the lemon oils of Messina and Palermo contain *geranyl acetate*. From socalled concentrated oils, *i. e.* from the high-boiling fractions rich in oxygen, they removed the aldehydes with hot bisulphite solution and saponified the non-aldehyde constituents. From the alkaline solution they separated acetic acid, and from the oil a fraction which formed a solid derivative with calcium chloride and which upon oxidation yielded citral. Hence they regard it as geraniol, which occurs in the original oil as acetate. From Palermo lemon oil they isolated, in addition to geraniol, a fraction having the properties of *l*-linalool. Umney and Swinton are of the opinion that the differences in the odor of the lemon oils from Palermo and Messina are due not only to the differences in the ratio between citral and citronellal of the two oils, but also to the presence of *linalyl acetate* in the Palermo oil.

15. *Bisabolene.* The occurrence of a sesquiterpene in lemon oil was first pointed out by V. Oliveri [4]). Schimmel & Co. [5]) determined the constants of this hydrocarbon and pointed out its remarkably low specific gravity. H. E. Burgess and T. H. Page [6]) obtained a hydrochloride melting at 79 to 80° and established its identity with the *limene* previously obtained by them from oil of limes. The identity of both sesquiterpenes with the known

[1]) Report of Schimmel & Co. October 1902, 40.

[2]) Bericht von Schimmel & Co. October 1888, 17.

[3]) Pharmaceutical Journ. 61 (1898), 196 and 370.

[4]) Gazz. chim. ital. 21, I (1891), 318; Berl. Berichte 24 (1891), 624, abstracts.

[5]) Bericht von Schimmel & Co. October 1903, 26.

[6]) Journ. chem. Soc. 85 (1904), 416.

bisabolene, previously isolated from Bisabol myrrh[1]) was established by Gildemeister and Müller[2]).

16. *Cadinene.* Bisabolene is accompanied by a higher boiling sesquiterpene which likewise yields a hydrochloride. On account of the small amount available, its melting point could by recrystallization not be brought higher than 110 to 113°, but all of its properties suggested cadinene.

17. *Acids.* According to von Soden and Rojahn[3]) acids can be removed from lemon oil by shaking it with sodium bicarbonate solution. When the solution of sodium salts is acidulated with sulphuric acid and shaken with ether a small amount of acids is obtained, which are in part volatile in part non-volatile. The latter shows a light blue fluorescence and dissolves in alkali carbonates with a beautiful light blue color.

E. J. Parry[4]) is of the opinion that traces of the *methyl ester* of *anthranilic acid* are present in the oil.

18. *Citroptene, citraptene or lemon camphor.* Upon prolonged standing the expressed lemon oil separates a waxy, soft, more or less slimy mass, which likewise remains as a yellowish-brown residue when the oil is rectified or evaporated. Concerning its composition there exists an extensive literature[5]). E. Schmidt[6]), however, first succeeded in revealing the constitution of *citroptene* which is identical with limettin. Upon treating the distillation residues of *lemon oil* with ether, citroptene is obtained as a granular, crystalline mass. It is insoluble in ether and after repeated crystallization from acetone and methyl alcohol, and finally from dilute alcohol to which animal charcoal has been added, it is obtained as shiny, colorless needles that melt at 146 to 147 . The solutions reveal a handsome violet blue fluo-

[1]) Comp. W. Tucholka, Arch. der Pharm. 235 (1897), 292.

[2]) Wallach-Festschrift, Göttingen 1909, p. 448. — Report of Schimmel & Co. October 1909, 64.

[3]) *Loc. cit.*

[4]) Chemist and Druggist 56 (1900), 993.

[5]) G. J. Mulder, Liebig's Annalen 31 (1839), 69. — W. Tilden and C. Beck, Journ. chem. Soc. 57 (1890), 328; Berl. Berichte 23 (1890), 500, abstracts. — L. Crismer, Bull. Soc. chim. III. 6 (1891), 30; Berl. Berichte 24 (1891), 661, Referate. — E. Theulier, Rev. gén. de Chim. 3 (1900), 421. — H. E. Burgess, Proceed. chem. Soc. 17 (1901), 171.

[6]) Apotheker Ztg. 16 (1901), 619. — Arch. der Pharm. 242 (1904), 288.

rescence. Analysis reveals the composition $C_{11}H_{10}O_4$ and meth-oxyl determinations, the presence of two methoxylgroups. Fusion with potassa yields *phloroglucinol* and *acetic acid*. In chloroformic solution citroptene combines with bromine to form a *dibromide* $C_{11}H_{10}Br_2O_4$, that melts between 250 and 260°. The supposition that citroptene is a methylated *dihydroxy cumarin* was confirmed by synthesis. Starting with *phloroglucinol,* Schmidt converted this into *phloroglucin aldehyde* and from this, upon cumarin synthesis, a dihydroxy cumarin which, upon methylation, yielded a compound corresponding in its properties with citroptene. It melted at 146 to 147°. Hence citroptene is represented by the following formula.

$$H \quad OCH_3$$
$$CH_3O \cdot \quad \cdot CH \quad CH$$
$$H \quad O \cdot CO$$
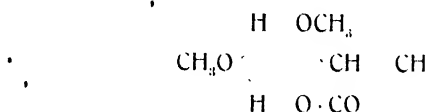
In addition to citroptene and other compounds, Schmidt found in the lemon oil residues a phenol melting a 89° which dissolves in sulphuric acid with a deep red color but does not react with ferric chloride.

Examination. The examination of lemon oil as to its purity is one of the most difficult tasks of the analytical chemist. As has already been pointed out, the properties of the oils vary considerably with the districts in which they are produced, also with the periods of the year in which the fruit is harvested. To these difficulties there should be added the uncertainty to detect the addition of hydrocarbons which result upon the pro-duction of terpene-free oils, provided this addition is restricted to certain limits. A further difficulty exists in the presence of non-volatile substances which interfere with the isolation and assay of such constituents as citral. Indeed, the citral assay of lemon oil is one of the most difficult tasks. Because of the low citral content of this oil, its assay must be extremely exact in order to utilize the results as a means of detecting the additions of non-aldehydic substances. It should furthermore be remembered that adulterators can readily bring the citral content of an adulterated oil up to the required standard.

Gross adulterations can be detected by the determination of the specific gravity and angle of rotation. Important con-

clusions can also frequently be drawn from the amount of evaporation residue. Adulterations with turpentine oil can be detected in most instances by a comparison of the optical rotation of the first 10 p.c. of distillate with that of the original oil. The solubility test according to G. Patanè (comp. p. 45) has not yet been corroborated sufficiently by experience to judge its value. Neither has the viscosity determination (see p. 47) found its way into practice.

METHODS OF CITRAL ASSAY.

1. The first attempt to determine quantitatively the amount of citral in lemon oil was made by H. Garnett[1]), who reduced the aldehydes to alcohols by means of sodium and attempted to assay the latter by acetylation. As detailed experiments have revealed, the reaction is unfortunately not quantitative, hence the results are useless[2]).

2. *Method of J. Walther.* Walther[3]) has utilized citraloxime for the quantitative determination of this aldehyde. An alcoholic solution of hydroxylamine hydrochloride of known strength is boiled with a definite amount of lemon oil (about 10 g.) and some sodium bicarbonate for three-fourths of an hour on a water bath in a long-necked flask connected with a reflux condenser. After cooling, the amount of unconsumed hydroxylamine hydrochloride in the reaction mixture is determined titrimetrically with $\frac{N}{10}$ sodium hydroxide solution. The difference between the amount of hydroxylamine hydrochloride originally employed and that thus found represents the amount that has entered into reaction with the citral and admits of the computation of the latter. On account of the inaccurate results the method has not been, followed[4]). For this reason it has been modified by A. H. Bennett[5]). In order to avoid the evolution of carbon dioxide, and with it the occasional loss of hydroxylamine, he has employed caustic potassa in place of sodium bicarbonate. The amount of alkali is chosen so that an excess of hydroxylamine with reference to the citral

[1]) Chemist and Druggist 48 (1896), 599.

[2]) Report of Schimmel & Co. October 1896, 41.

[3]) Pharm. Zentralh. 40 (1899), 621; 41 (1900), 585.

[4]) Report of Schimmel & Co. April 1900, 22 and October 1901, 26.

[5]) Analyst 34 (1909), 14; Chem. Zentralbl. 1909, I. 593.

is liberated from its hydrochloride, but that some of the hydro-
chloride remains unchanged. To a mixture of 20 cc. of lemon
oil and 20 cc. $\frac{N}{2}$ alcoholic (80 p.c.) hydroxylamine hydrochloride
solution, 8 cc. alcoholic normal potassium hydroxide solution and
20 cc. of aldehyde-free strong alcohol are added and the mixture
boiled for one-half, hour in a flask connected with a reflux
condenser. After the reaction mixture has cooled, 250 cc. of
water are added, part of which is used to rinse the reflux
condenser, and the hydrogen chloride still combined with the
hydroxylamine is neutralized, phenolphthalein being used as
indicator. The hydroxylamine not combined with the citral is then
titrated with $\frac{N}{2}$ sulphuric acid, the end reaction being ascertained
by removing drops to be tested with methyl orange as indicator.
A blind is conducted in like manner but without lemon oil in
order to'ascertain the factor of the hydroxylamine solution. From
the difference in the half-normal sulphuric acid consumed in the
two experiments the amount of hydroxylamine that has entered
into reaction can be ascertained and the amount of citral can be
computed by multiplication with 0.076. The serviceability of the
method was determined by Bennett by using pure citral. When
lemon oil was tested the citral content fluctuated between 4.3
and 5.2 p.c.

    Schimmel & Co.[1]) found that by adding pure citral to the
oil the results were too low by 10 p.c.

    3. *Method of A. Soldaini and L. Berte*[2]). 5 cc. of lemon oil
are measured at a definite temperature in a cylindrical pipette
graduated into $\frac{1}{40}$ cc. and allowed to flow into a 100 cc. fractionating
flask, the neck of which is so contracted that it can be connected
with the inverted pipette by means of a rubber tube. The lateral
tube of the fractionating flask is bent upward and can be closed
by means of a piece of rubber tubing and pinch cock. To the
oil in the fractionating flask 25 cc. of a·saturated solution of
potassium acid sulphite solution, containing some free acid, are
added and the mixture shaken thoroughly. The mixture is then

    [1]) Report of Schimmel & Co. October 1909, 153.

    [2]) *Metodi generali per l'analisi delle essenze ed in particolare per le
essenze esperidee.* Boll. chim. farm. 38 (1899), 537; Report of Schimmel & Co.
April 1900, 25.

digested for 10 minutes in a boiling water bath, care being taken
to shake the flask at short intervals and to see to it that it does
not become hotter than is convenient to the touch if the bulb
is held in the hand. The contents are then allowed to cool with
constant shaking, again heated for 5 minutes and finally allowed
to cool completely without interruption in the shaking. The
lateral tube is now connected with a funnel, through which water
can be added as desired to the flask, and the inverted cleansed
and dried pipette is connected by means of a rubber tube with
the upper, contracted end of the fractionating flask. Water is
now added through the funnel and, assisted by rotation and
rapping, the floating oil is induced to rise into the pipette. For
the purpose of removing any oily particles that adhere to the
neck, air is forced through the lateral tube. The air will carry
with it any oil. After all of the oil has thus been collected in
the pipette, it is allowed to become clear by standing and its
volume read off and the difference computed as volume of citral.
For the determination of the approximate percentage by weight
an average specific gravity of 0.850[1]) is taken.

This method has proven inexpedient because at the border
of the oily and aqueous zones a mucilaginous and salty secretion
is formed which renders an exact reading impossible.

4. *Method of E. J. Parry.* Parry[2]) has suggested to determine
the citral content of lemon oil with the aid of the citrylidene
cyanacetic acid discovered by Tiemann. From 200 cc. of lemon
oil, about 175 cc. are removed by fractional distillation under
diminished pressure. The residue is measured and the temperature
noted. To 10 cc. thereof contained in a cassia flask a solution
of 5 g. of cyanacetic acid in 30 g. of 15 p.c. sodium hydroxide
solution are added and the mixture shaken at a low temperature.
The aldehyde of the oil dissolves in the aqueous-alkaline liquid,
whereas the non-aldehyde constituents float on the solution. The
volume of the latter is read off in the graduated neck of the
flask at the same temperature at which the volume of the residue
of the oil was determined. The number of cc. read off is
deducted from 10. This difference with reference to the original

[1]) Apparently a printer's error, and should read 0.859.
[2]) Chemist and Druggist 56 (1900), 376.

liberated sodium hydroxide with the acid, the original red color produced by the rosolic acid gradually passes over into pink, hence it is difficult to decide which shade of color is to be regarded as indicating the end of the reaction. Neither will it do to titrate the solution until an absolute change in color takes place for then the results obtained 'are several percent too high [1]).

6. *Method of G. Romeo*[2]). This method is very similar to Sadtler's and suffers from the same defect, *viz*. that the end reaction cannot be determined accurately. In trying out the method it was not even possible to standardize the solution accurately according to directions [3]).

This method is based on the reaction of citral with a solution of neutral and acid sulphite with the formation of a trihydro-trisulphonic acid according to the following equations: —

1. $C_uH_{15} \cdot C_O^H + \begin{matrix} 2\,Na_2SO_3 \\ NaHSO_3 \end{matrix} + 2H_2O$

   $C_uH_{17} \cdot (SO_3Na)_2 \cdot CH(OH)SO_3Na + 2\,NaOH.$

2. $2\,NaOH + 2\,NaHSO_3 - 2\,H_2O + 2\,Na_2SO_3.$
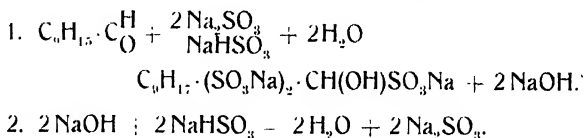
According to the above equations three acid equivalents correspond to one molecule of citral. For the assay a solution of 400 g. $Na_2SO_3 + 7\,H_2O$ in 1 liter of water $+$ 160 cc. of a concentrated potassium acid sulphite solution are standardized against $\frac{N}{2}$ potassium hydroxide. 25 cc. of this are gently heated with 5 cc. of lemon oil, titrated with acid, rosolic acid being used as indicator, and the citral content computed. Experiments were made with pure citral, solutions of citral in xylene of known aldehyde content, and citral-containing oils (ordinary as well as terpene-free). The results obtained by the author agree very well. Four lemon oils revealed a citral content varying between 3.64 and 4.48 p.c.

R. O. Brooks[4]) employs a neutralized potassium bisulphite solution in place of that of sodium sulphite. However, according

[1]) Report of Schimmel & Co. April 1914, 48.

[2]) *Un nuovo metodo di determinazione quantitativa del citral*. Messina 1905.

[3]) Report of Schimmel & Co. October 1905, 30.

[4]) Americ. Perfumer **3** (1908), 24.

to Schimmel & Co.[1]), this modification does not remove the defects of the method.

7. *Method of P. B. Rother*[2]). This method for the assay of aldehydes and ketones is based on their conversion into phenyl-hydrazones, the reaction of the excess of phenylhydrazine with iodine, and finally *the titration of the excess of iodine with thiosulphate. According to E. Fischer the reaction between iodine and phenylhydrazine is expressed by the following equation: -

$$2 C_6H_5NHNH_2 + 2I_2 = C_6H_5N_3 + C_6H_5NH_2 \cdot HI + 3 HI.$$
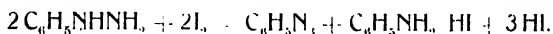
However, according to E. von Meyer, the reaction is modified by an excess of iodine as expressed by the following equation:

$$C_6H_5NH \cdot NH_2 + 2I_2 = C_6H_5J + N_2 + 3 HI.$$
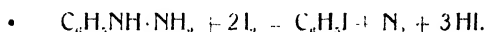
Fully 5 g. of phenylhydrazine are dissolved in about 250 cc. of warm water, the solution filtered to remove resinous products into a half-liter flask. After cooling the flask is filled to the neck with boiled distilled water. The rather unstable solution is to be kept well stoppered and away from light.

The strength of the phenylhydrazine solution is determined in the following manner: 300 cc. of water and exactly 40 cc. of $\frac{N}{10}$ iodine solution are transferred to a liter flask. With the aid of a pipette, 10 cc. of the phenylhydrazine solution are transferred to a small flask containing 50 cc. of water and the diluted solution transferred to the liter flask. After about 1 minute the excess of iodine is titrated with $\frac{N}{10}$ thiosulphate. 0.1 g., of pure phenyl-hydrazine corresponds to 37 cc. of $\frac{N}{10}$ iodine solution.

Of the lemon oil to be examined, about 10 g. are weighed in a weighing flask and in order to avoid oxidation several cc. of alcohol are immediately added. With the aid of about 30 cc. of alcohol the oil is then transferred to a flask of 250 cc. Enough standardized phenylhydrazine solution is then added so as to supply one molecule of phenylhydrazine for every molecule of aldehyde or ketone. The mixture is then thoroughly shaken and set aside for about 20 hours protected against light and

[1] Report of Schimmel & Co. October 1905, 156.
[2] *Die Bestimmung der Aldehyde und Ketone zur Bewertung ätherischer* Inaug. Dissert. Dresden 1907.

repeatedly shaken during this time. After this the unchanged
oil is removed by means of a separating funnel and repeatedly
washed with water, the washings being added to the liquid to
be titrated. This liquid is still further diluted with water and
filtered through a pleated filter (if necessary with some gypsum),
into a liter flask containing about 500 cc. of water and 10 to
20 cc. of $\frac{N}{10}$ iodine solution, the latter amount varying according
to the amount of phenylhydrazine used. During the process of
filtration the flask is shaken repeatedly. The filter having been
carefully washed with water, the liquid is titrated with $\frac{N}{10}$ thio-
sulphate solution, starch solution being used as indicator.

The percentage of aldehyde being indicated by x, this can
be computed with the aid of the following formula: —

$$x \quad \frac{d \cdot M}{100 \cdot 4 \cdot s} ,$$

in which d is the difference between the amount of cc. of $\frac{N}{10}$
iodine solution corresponding to the phenylhydrazine used and
the actual number of $\frac{N}{10}$ iodine solution consumed, M the mole-
cular weight, and s the amount of material used expressed in grams.

Upon trying out this method[1] it was found that, in general,
useful results are obtainable but that these do not exceed in
accuracy those obtained by the volumetric bisulphite method
and the sulphite method. In daily practice it offers no advantage
over the other two methods, both because of the instability of
the required solutions and because it takes too long to ascertain
the results. Neither is the method sufficiently reliable so that
conclusions as to the quality of the oil can be drawn directly
from the determined citral content. Indeed, the variations in
the results are sufficiently large to admit of the passage of
adulterated oils as good ones.

8. *Method of P. Bruylants.* For a long time the blood spectrum
has been employed for the detection of such substances as oxygen,
carbon monoxide and hydrogen cyanide by observing the change
in the spectra produced by them. Recently Bruylants[2] has utilized
the spectroscopic behavior of the blood for the quantitative deter-

[1] Report of Schimmel & Co. October 1907, 121.
[2] Bull. de l'Acad. roy. de Belgique *(Classe des sciences)* 1907, 217, 955. —
Annal. de Pharm. 13 (1907), 321.

·mination of aldehydes proceeding from the following considerations.
If yellow ammonium sulphide and a small amount of aldehyde
are added to defibrinated blood, the two absorption bands of
the oxyhæmaglobin loose their intensity. Gradually a third band
appears between them which increases in distinctness and ulti-
mately acquires the, same degree of intensity as the two bands
of the oxyhæmaglobin. These are then modified still more.
Bruylants points out that, according to his method, not only the
citral but all of the aldehydes are determined in the lemon oil.
So far as practical results are concerned this is of little con-
sequence since the other aldehydes are present in small amount
only as compared with citral.

For carrying out the determination the following instruments
and reagents are needed: 1. A spectrophotometer after d'Arsonval
the two fields of vision of which are arranged one above the
other so as to admit of direct comparisons; also the containers
for solutions belonging thereto, burettes and test tubes. 2. A
3 p.c. blood solution, made from fresh, defibrinated pig's blood,
which in the spectroscope shows the two bands characteristic
of oxyhæmaglobin. 3. A solution of ammonium sulphide which
must be prepared with special care in order to obtain the desired
results. (A definite volume of ammonia is saturated with hydrogen
sulphide, a somewhat larger volume of ammonia is added, and
the ammoniacal sulphide solution thus obtained exposed to the
light for several days.) 4. Citral solutions of 3, 4 and 5 p.c.
citral in citral-free oil for comparison. 5. Aldehyde-free, 94 p.c.
alcohol prepared by boiling over potassium hydroxide and
m-phenylenediamine hydrochloride.

Preliminary tests are made preferably by two persons to
ascertain the approximate percentage of aldehyde. To 9 cc.
each of the blood solution, 1 cc. of the ammonium sulphide
solution is added, and then the solution of the oil to be examined
to the one and the 5 p.c. citral control solution to the other.
The solutions' should be prepared under exactly the same con-
ditions. Both of the oil solutions are so prepared that for
every cc. of aldehyde-containing oil 5 cc. of alcohol are used.
At first 0.15 cc. of each solution is added and the containers
shaken for about one-half minute. After separation of the in-
soluble portions, the lower layer is removed by means of a

pipette and transferred to the spectroscope tubes. When working fairly rapidly the oxyhæmaglobin bands can be located in both fields of vision. Then the band in the middle appears as first phase of the reaction. If the aldehyde content is the same in both solutions this middle band appears in both fields at the same time. If this is not the case the amount of the alcoholic solution of the oil is increased or diminished by one-hundredth part of a cc. whereas the amount of the control solution remains the same. Thus, after 5 or 6 tests the aldehyde content can be ascertained approximately. In the subsequent exact determination, a control solution is used, the aldehyde content of which approximates that of the oil to be examined. If the oil contains less than 5 p.c. aldehyde, a 3 or 4 p.c. citral solution is used; if more than 5 p.c., the 5 p.c. solution is employed and the solutions are tested until the middle absorption band appears at the same time. After some practice, a complete determination can really be made within a half hour. The results are fairly exact. In an artificial oil with 5.06 p.c. of citral, 4.9 p.c. were found.

Several lemon oils were examined by Bruylants and the following volume percentages of citral ascertained:

Messina oil, 1906 harvest: 4.58 and 4.65 p.c.; harvest of January 1905: 5.42 and 5.52 p.c.; harvest of November 1904: 6.47 p.c.

Reggio oil, 1906 harvest: 5.10 and 5.14 p.c.

Two commercial oils contained 3.5 and 3.7 p.c., a third contained but 2.86 p.c. citral.

Whatever the scientific interest may be that is attached to this method, from the point of view of the analytical laboratory it is much too complicated to be used in the assay of volatile oils. For this reason it apparently has not been used in practice.

9. *Method of E. M. Chace*[1]). This method is based on the property of fuchsinsulphurous acid to become red in the presence of aldehydes, the intensity of the red color depending on the amount of aldehyde present. A comparison with the color of solutions of known aldehyde content enables the determination of the aldehyde in the oil to be examined.

[1]) A method for the determination of citral in lemon oils and extracts. Journ. Americ. Chem. Soc. 28 (1906), 1472.

The following reagents are required: 1. Fuchsinsulphurous acid: ·0.5 g. fuchsin are dissolved in 100 cc. of water and a solution containing 16 g. of sulphurous acid is added. When decoloration has taken place, the solution is diluted to 1 liter. This solution has to be prepared fresh every 2 or 3 days since it spoils readily. 2. Alcohol of 95 p.c. by volume that is absolutely free from aldehydes. In order to remove all but traces of the aldehyde, the alcohol is allowed to stand over alkali. The alcohol is then distilled and the distillate boiled for several hours with m-phenylenediamine hydrochloride, using 25 g. per liter. After a second distillation the alcohol is ready for use. 3. A standard citral solution, *i. e.* a solution of 0.1 p.c. of citral in 50 p.c. aldehyde-free alcohol. These, as well as the following solutions, are prepared at a temperature of 15 . At this temperature all of the determinations are made, the several containers being kept at this temperature in a waterbath for ten minutes before being used. Above all, a higher temperature is to be avoided.

The assay is carried out in the following manner: 2 g. each of the oils to be examined are diluted to 100 cc. with aldehyde-free alcohol. 4 cc. each of these solutions are transferred to flasks of the same size, 20 cc. aldehyde-free alcohol added and then 20 cc. of fuchsinsulphurous acid and the solution diluted to 50 cc. with alcohol and well mixed. With the standard citral solution, like solutions are made for comparison. All solutions are allowed to remain in the water-bath for 10 minutes when the intensity of the colors are compared either directly or with the aid of a colorimeter.

As tried out by Chace, this method yields fairly satisfactory results with mixtures of citral and limonene, the values found differing not more than 0.2 p.c. on the average from the real citral content. With lemon oils the results were not as favorable though here also the errors remained within 0.5 p.c.

While trying out this method, Schimmel & Co.[1] did not use the colorimeter, but compared the intensity of color directly. They prepared eight different mixtures of the standard citral solution with the fuchsinsulphurous acid and alcohol in such a

[1] Report of Schimmel & Co. April 1907, 116.

manner that each subsequent mixture contained 1 cc. solution — 1 mg. citral more that the preceeding one: the first mixture containing 1 cc. of standard solution · 1 mg. citral, the eighth one 8 cc. of solution 8 mg. citral. Thus it became apparent that up to 5 mg. citral content the mixtures revealed differences in color, whereas beyond 5 mg. the color become so intense that differences were no longer observable. Smaller differences than 1 mg. in the citral content of the solutions were directly observable *i. e.* without colorimeter, only in very dilute solutions, *i. e.* up to about 2 mg. citral.

According to Schimmel & Co. the citral content of *lemon oils* cannot be determined with certainty in this manner, since the waxy constituents of the oil prevent the recognition of the tone of color with any distinctness. This results in appreciable errors. The amount of citral found by the comparison of colors is to be multiplied by 1250 to yield the citral content of the oil. If there is any doubt as to whether the color indicated a citral content of 3 mg. or 4 mg. (lesser differences cannot be determined for lemon oil) the following percentages result: 0.003·1250 3.75 or 0.004·1250 5.0, hence results that differ by 1.25 p.c. For the low citral content of lemon oils this difference is too great for the oils themselves, though, no doubt, the method is applicable to lemon extracts. Indeed Chace himself has expressed this view in his publication.

10. *Method of R. S. Hiltner*[1]). For the determination of citral in lemon extracts and oils Hiltner likewise recommends a colorimetric method. It is based on the observation that at room temperature the addition of citral to a dilute alcoholic solution of *m*-phenylenediamine hydrochloride causes the formation of a yellow color, the intensity of which increases with the citral content. For this purpose a 1 p.c. freshly prepared solution of *m*-phenylenediamine hydrochloride in 50 p.c. alcohol is employed. It must be perfectly colorless and clear, conditions that are attained, if necessary, by treatment and filtration with animal charcoal. By comparison with a solution of known citral content (0.25 g. citral to 250 cc. of 50 p.c. alcohol), the citral content of an extract or oil can be determined.

[1]) Journ. ind. eng. Chemistry 1 (1909), 798; Chem. Zentralbl. 1910, I. 1899.

For a determination 1.5 to 2.0 g. of lemon oil are diluted with 90 to 95 p.c. alcohol to make a 50 p.c. solution. Of this solution 2 cc. are transferred to the colorimeter tube, 10 cc. of the phenylenediamine solution are added, and the mixture diluted to a definite volume. With the standard citral solution comparative mixtures are prepared until the same intensity of color has been produced as has resulted in the solution of the oil to be tested. From this the citral content of the oil can be computed.

If, according to directions, the tests are made at room temperature the reaction is influenced neither by the acetaldehyde of the alcohol, nor by the other constituents of the oil. However, for oils that have been altered by oxidation, the method cannot be used, for such oils, according to the degree of oxidation, produce a yellowish-green to greenish-blue color.

11. *Method of C. Kleber[1]).* Even before its publication this method had been used for a longer period by Schimmel & Co.[2]) who tested it as to its utility. It was thus demonstrated that it is superior to all methods published hitherto, not only because it yields more reliable results, but also because it can be carried out more readily. It is based on the observation that phenylhydrazine can be titrated accurately with mineral acids when ethylorange is used as indicator and that the hydrazones which the phenylhydrazine forms with aldehydes and ketones react neutral toward ethylorange. Inasmuch as the phenylhydrazine solution decomposes very rapidly, it is best prepared fresh for each assay. At least no solution should be employed that is more than one day old. If necessary the phenylhydrazine is previously distilled in vacuum.

According to the directions, slightly modified by Schimmel & Co., about 2 g. of oil are mixed with a freshly prepared 2 p.c. alcoholic phenylhydrazine solution in a 50 cc. glass-stoppered flask and set aside for 1 hour. Then 20 cc. of $\frac{N}{10}$ hydrogen chloride are added and the liquids mixed by gentle shaking. 10 cc. of benzene are then added and after the mixture has been shaken thoroughly it is transferred to a separating funnel.

[1]) Americ. Perfumer 6 (1912), 284.
[2]) Report of Schimmel & Co. April 1912, 75.

After having been allowed to stand for a short time, the 30 cc. of acid layer are drawn off and filtered through a small filter.

20 cc. of this filtrate to which 10 drops of ethylorange solution (1:2000) have been added, are titrated with $\frac{N}{10}$ potassium hydroxide until a distinct yellow color appears. From this the amount of $\frac{N}{10}$ potassium hydroxide required for 30 cc. of filtrate is computed. For the standardization of the phenylhydrazine solution a blind experiment *i. e.* without oil is made. If the 30 cc. of filtrate of the first experiment demands a cc. of $\frac{N}{10}$ potassium hydroxide and b cc. in the latter experiment, the citral equivalent of the amount of oil (s grams) used is $a-b$ cc. $\frac{N}{10}$ potassium hydroxide. In as much as 1 cc. of $\frac{N}{10}$ potassium hydroxide corresponds to 0.0152 g. of citral, the percentage content of the oil can be computed with the aid of the following formula

$$\frac{(a-b)\cdot 1.52}{s}$$

The object of shaking out with benzene is to render clear the solution which has become turbid upon addition of the hydrogen chloride. This facilitates the recognition of the change in color.

In the following table are recorded the results obtained by this method with mixtures of known citral content. These clearly reveal the usefulness of the method: —

	Citral content of the solution.			
	2 p.c.	4 p.c.	6 p.c.	7.3 p.c.
Found	2.4 p.c.	4.1 p.c.	6.2 p.c.	6.9 p.c.
	2.0 „	4.0 „	5.9 „	7.0 „
	—	3.9 „	6.0 „	7.1 „

A comparison of the results obtained according to the several methods for the assay of citral reveals appreciable differences. Hence it is always necessary to report the method with the results. The citral content of pure or supposedly pure oils is recorded by the following investigators: — Soldaini and Bertè[1]: 6.5 cc. in 100 cc. oil; Parry[2]: 5 to 6 p.c.; Parry[3]: 3 p.c.;

[1] Boll. Chim. Farm. 38 (1899), 537; Report of Schimmel & Co. April 1900, 25.
[2] Chemist and Druggist 56 (1900), 376.
[3] *Ibidem* 63 (1903), 820.

Sadtler[1]): 5.26 p.c.; Bertè[2]): 6.85 to 7.4 p.c.; Romeo[3]): 3.64 to 4.48 p.c.; Rother[4]): 5.25 to 5.9 p.c.; Bruylants[5]): 2.86 to 6.47 p.c.; A. H. Bennett[6]): 4.3 to 5.2 p.c.; Chace[7]): 4.1 to 7.0 p.c.

Determined according to Kleber's method, which is pronounced the most reliable by several American chemists[8]), the citral content of pure lemon oils varies between 3.5 and 5 p.c. and is mostly about 4 p.c.[9]). Hence the citral content in different oils fluctuates by more than 70 p.c. For this reason the citral content admits of the detection of adulteration only then when this is considerable. Thus to an oil which originally contained 5 p.c. of citral 20 p.c. of non-aldehyde constituents might be added without detection by this means. Nevertheless, the citral assay is indispensable in the valuation of a lemon oil.

THE DISTILLATION TEST is used principally for the detection of turpentine. In spite of the addition of turpentine oil, an adulterated oil of lemon may reveal a normal optical rotation provided the reduced rotation is compensated by the addition of orange oil. Such and adulteration may, however, be detected by the optical examination of special fractions of the oil. In the case of pure oils, the angle of rotation of the first 10 p.c. of distillate is but 5 to 6° lower than that of the original oil[10]). For oils to which turpentine oil has been added the difference is greater. For this distillation test a Ladenburg fractionating flask with three bulbs (fig. 71, p. 566 of vol. I) is used. From 50 cc. of the oil to be examined exactly 5 cc. are distilled. A few drops of water pass over first and render the distillate turbid.

[1]) Americ. Journ. Pharm. 76 (1904), 84.

[2]) Chem. Ztg. 29 (1905), 805; Chemist and Druggist 66 (1905), 682.

[3]) Un nuovo metodo di determinazione quantitativa del citral. Messina 1905; Report of Schimmel & Co. October 1905, 30.

[4]) Die Bestimmung der Aldehyde und Ketone zur Bewertung ätherischer Öle. Inaug. Dissert., Dresden 1907.

[5]) Bull. de l'Acad. roy. de Belgique (Classe des sciences), N°3, 1907, 217. — Annal. de Pharm. 13 (1907), 321.

[6]) Analyst 34 (1909, 14; Report of Schimmel & Co. April 1909, 110.

[7]) Journ. Americ. chem. Soc. 28 (1906), 1472.

[8]) E. M. Chace U. S. Dep. of Agricult., Bureau of Chemistry, Bull. N° 137 (20. July, 1911), p. 64.

[9]) Comp. Report of Schimmel & Co. April 1914, 58.

[10]) In one instance Chace observed as high as 6.17′.

These can be removed by shaking with anhydrous sodium sulphate. After filtration the distillate is examined in a 50 mm. polariscope tube, the temperature having been observed accurately. The result is computed for 20° in accordance with the directions given in footnote 1 on p. 17 and deducted from the result obtained for the original oil likewise computed for 20°[1]).

In certain instances, more particularly when the amount · of available oil is but small, the modification of Soldaini and Bertè [2]) is preferable. This consists in distilling off one-half from 25 cc. of oil. In the case of pure oils, the optical rotation of the 50 p.c. of distillate is higher than that of the original oil, likewise than that of the residue. In the case of adulteration with turpentine oil, that of the first half is invariably lower.

This modification, however, is no better than the original Schimmel's test which, in an emergency, can be conducted with 25 cc. of oil. For the detection of the addition of lemon oil terpenes both methods fail [3]). The suggestion made by H. E. Burgess [4]) to distil under diminished pressure does not afford any particular advantages.

DETECTION OF PINENE ACCORDING TO CHACE. Assuming that pure turpentine oil is at most to contain but traces of pinene, E. M. Chace [5]) has published a method which is to enable the detection of mere traces of turpentine oil. It is based on the observation that the nitrosochloride of pinene and limonene crystallize in different forms readily recognizable under the microscope. Whereas the pinene derivative separates in laminæ, the limonene derivative crystallizes in needles. Chace proceeds in the following manner: -

From 50 cc. of oil contained in a Ladenburg flask, he fractionates 5 cc. From this, with the aid of ethyl nitrite, he prepares the nitrosochloride according to Wallach's method. The

[1]) Report of Schimmel & Co. October 1896, 39.

[2]) Gazz. chim. ital. 27, II. (1897), 25.

[3]) Comp. also Bertè, Boll. Chim. Farm. May 1904, No. 10; Report of Schimmel & Co. October 1904, 29. · Chemist and Druggist 66 (1905), 713.

[4]) Chemist and Druggist 75 (1909), 946.

[5]) Journ. Americ. chem. Soc. 30 (1908), 1475; Report of Schimmel & Co. October 1908, 64. -- The occurrence of pinene in lemon oil. U. S. Department of Agriculture, Bureau of Chemistry, Circular No. 46. 30. October 1909.

reaction mixture is allowed to remain 15 minutes in the freezing mixture when the crystals are removed by means of a suction filter, and washed with 50 cc. of 95 p.c. alcohol. The mother liquid is exposed another 15 to 20 minutes to the temperature of the freezing mixture. The second crop of crystals is united with the first. The united crystals are washed well with alcohol, dried and dissolved in the smallest possible amount of chloroform. Enough hot methyl alcohol is then added to result in crystallization upon cooling. Finally somewhat more methyl alcohol is added and the crystals removed by filtration. For testing under the microscope, the crystals are best mounted in olive oil. In this manner Chace could detect an addition of 2 p.c. of turpentine oil whereas with the aid of a three-bulb Glinsky fractionating column even 0.5 p.c. of added turpentine oil could be detected. Additions of 10 to 15 p.c. could be detected by preparing the nitrosochloride from the *original* oil.

Both J. C. Umney [1]) and Parry [2]) have protested against the usefulness and applicability of this method. Wiley [3]), however, justifies it by the claim that since its application by the Bureau of Chemistry of the U. S. Department of Agriculture not a single imported oil has had to be questioned.

It is necessary, however, to follow the directions. In the case of the isolation of but small amounts of pinene nitrosochloride, the oil should be allowed to pass and questioned only then if larger amounts are obtained.

PATANÈ'S METHOD FOR DETERMINING THE AMOUNT OF THE CONSTITUENTS SOLUBLE IN DILUTE ALCOHOL. As is well known, lemon oil consists largely of terpenes and sesquiterpenes which are of but little value so far as the odor is concerned. Whereas these hydrocarbons are all but insoluble in 80 p.c. alcohol, the valuable odoriferous constituents are soluble therein. Hence G. Patanè [4]) regards the determination of the solubility as a valuable criterion in judging an oil and has based thereon a

[1]) Brit. and Colon. Druggist 1909, 447; Report of Schimmel & Co. April 1910, 66.

[2]) Chemist and Druggist 75 (1909), 875. - Americ. Perfumer 4 (1910), 214.

[3]) Chemist and Druggist 75 (1909), 913. - Americ. Perfumer 4 (1910), 226.

[4]) *Per un più razionale apprezzamento delle essenze di limone.* Acireale 1912.

method of examination. Indeed, he employs two methods. The one consists in shaking thoroughly equal volumes of oil and alcohol of definite strength measured at exactly 20° in a 10 cc. cylinder graduated into 0.1 cc. After the two layers have separated, the increase in the volume of the alcoholic solution is noted. According to the other method, equal volumes of the oil and alcohol of definite strength are mixed in a test tube, and gently heated until solution has taken place. The solution is then allowed to cool, being constantly stirred with a thermometer, the scale of which is divided into tenths of degrees. As soon as the solution becomes turbid, the temperature is read off. Differences in temperature of one-tenth degree produce turbidity. All oils that reveal the same turbidity temperature show the same solubility according to the first method, hence a comparative scale between turbidity temperature and solubility can be prepared. In most instances it suffices to carry out the second test which is said to be rapidly executed and yet exact.

The addition of 10 p.c. of terpenes increases the turbidity temperature by more than one degree, that of 20 p.c. about two degrees, etc., with this difference, however, that with the increasing terpene content, the temperature intervals become smaller. In addition, the relation between citral content and solubility is said to admit of further conclusion as to the nature of the oil.

The alcohol used for this purpose must be standardized very carefully for the turbidity temperature varies with a difference in the strength of the alcohol of one-tenth of a degree. According to Patanè it is more expedient to use methyl alcohol in place of ethyl alcohol, since the oil is less soluble in the former. Inasmuch as the turbidity temperature in this instance lies above room temperature it is not necessary to cool the solution artificially as has to be done when ethyl alcohol of 93 to 94 p.c. strength is used.

Both tests can also be applied advantageously to the oils of orange and mandarin which are much less soluble than lemon oil. In the determination of the solubility it is necessary to consider the geographic source of the oil since differences in the soil influence the composition of the oil.

In order to judge the usefulness of this method more detailed experiments are necessary.

VISCOSITY DETERMINATION. According to E. Dowzard[1]) the ,...osity of the volatile oils is said to be an important aid in the determination of the purity or quality of volatile oils. Inasmuch as it seemed highly desirable to increase the means of ascer- taining the value of lemon oil, a number of viscosity determinations were carried out in the laboratory of Schimmel & Co.[2]) These are recorded in the accompanying table. The apparatus used was the same employed by Dowzard, *viz.* the viscosimeter of Reischauer. As unit of viscosity the time of flow of 25 cc. of water at 20° is indicated as 100. The viscosity number of the lemon oils tested is computed with the aid of the following formula.

$$V = \frac{O}{W} \times 100$$

where $O =$ the number of seconds required by the flow of 25 cc. of oil at 20°, and W the number of seconds required by the flow of 25 cc. of water at 20°.

So far as lemon oil is concerned, the experiments of Schimmel & Co. yielded no encouraging results. This is more particularly true of the addition of "citrene", for the values for "citrene" and lemon oil are too close to admit of the detection of this adulterant. Moreover, the difficulty of establishing standards is increased by the circumstance that different viscosimeters of the same make do not yield the same results, hence are not comparable. Whereas Dowzard found the viscosity number for pure lemon oil to be 139.6, the values found by Schimmel & Co. varied between 109.8 and 122.9. For "citrene" Dowzard found 105.8, Schimmel & Co. found 103.2.

The cause for these differences is to be looked for in the fact that the orifices of viscosimeter of this type are different. It may be possible to secure better results with more exact instruments that guard against this error. E. Quercigh and D. Moreschini[3]) regard the viscosimeter of O. Scarpa as suited for the determination of the viscosity of volatile oils. Another advantage of this instrument lies in the fact that smaller amounts of oil (1 to 5 cc.) suffice for the determination of exact results.

[1]) Chemist und Druggist 57 (1900), 168.
[2]) Report of Schimmel & Co. April 1901, 32.
[3]) Rendiconti della Società chimica ital. fasc. XIII. (1913); Report of Schimmel & Co. October 1913, 123.

The results obtained by Schimmel & Co. are recorded in the following table: —

Origin of the oil:	$d_{15°}$	$\alpha_{D20°}$	Viscosity at 20° (Water 100)
Messina I	0.8576	+ 61° 10′	120.0
„ hand pressed . .	0.8572	60° 18′	109.8
„ „ „ . .	0.8594	+ 61° 57′	114.6
„ machine pressed .	0.8574	61° 4′	122.9
„ hand pressed . .	0.8565	61° 27′	111.3
„ „ „ . .	0.8568	61 32′	112.0
„ „ „ . .	0.8583	62° 10′	111.3
Palermo I	0.8592	60° 20′	117.0
„ II	0.8591	59° 12′	121.0
Messina II	0.8568	61° 28′	113.6
Citrene from lemon oil from Palermo	0.8533	+ 65° 6′	103.2
„ Messina	0.8514	66° 35′	102.1
d-Limonene, crude	0.8528	101° 35′	100.9
Limonene, pure	0.8470	117° 40′	100.2
Citral, fresh.	0.8932	0°	201.4
„ old	0.8967	0	207.8

DETERMINATION OF THE HYDROCARBON CONTENT OF CONCENTRATED LEMON OILS ACCORDING TO E. BÖCKER[1]). This method consists in the removal, first of the citral by means of sodium sulphite, and then of the other aromatic substances by means of alcohol. The strength of the latter is chosen so that, with the observation of certain precautions, the hydrocarbons remain undissolved almost entirely. Böcker proceeds in the following manner:

The citral content of 10 cc. of oil is first examined according to the sulphite method (see vol. I, p. 584). If the volume of oil that does not enter into the reaction amounts to less than 6 cc. the assay is repeated with either 5 or 10 cc. The non-aldehyde constituents of both assays are united and 5 cc.

[1]) Journ. f. prakt. Chem. II. 89 (1914), 199.

thereof transferred to a 600 to 700 cc. separating funnel into which 500 cc. of 51 p.c. alcohol (by volume), cooled to from 0 to — 2°, have previously been placed. The separating funnel is stoppered with a cork and the contents are shaken repeatedly thus causing the aromatic constituents to go into solution whereas the hydrocarbons remain undissolved almost quantitatively. The inverted separating funnel (stopper downward) is then transferred to a bath of 0° in which it is allowed to remain for 8 to 10 hrs. After this time it is removed, carefully brought back to its normal position and suspended from a ring stand. After the alcoholic solution has become so clear that but a very faint turbidity remains, which may require up to two days, all but about 10 cc. of the liquid are drawn off. Any oil drops adhering to the separating funnel are washed down with ice-cold 50 p.c. (no doubt should read 51 p.c.) alcohol so that all dissolved oil is brought together. The separating funnel is again set aside until the alcohol has become wellnigh perfectly clear. After the last traces of alcohol have been separated so far as this is possible, the oil is transferred to a measuring cylinder, graduated into one-tenth cubic centimeters, the separating funnel being again rinsed with some ice-cold 51 p.c. alcohol. It is more practicable to use a separating funnel, the lower portion of which is drawn out to a narrow, calibrated tube. As soon as the oil has become clear (in case foam persists a few drops of dilute acetic acid are added), its volume is read off and the percentage with reference to the original oil computed.

If larger amounts of material are available, the quantitative determination can be supplemented by a qualitative examination of the separated hydrocarbons. For this purpose Böcker provides the following directions: 100 to 200 cc. of oil are fractionated in vacuum. The distillation is continued only so far as the fractions of 10 cc. each reveal dextrorotation. These are united as the terpene-containing portion of the oil whereas the remainder constitutes the sesquiterpene-containing portion of the oil. Both of these portions are now deprived of citral by means of sodium sulphite. The residual oils are treated separately as described above, with 100 times their volume of ice-cold 51 p.c. alcohol. If, desired glass bottles can be used in the place of the separating funnels, the alcohol being removed by

means of a siphon. The separated oils are measured and the terpene and sesquiterpene contents of the original oil computed. For further identification the optical rotation is ascertained and the characteristic derivatives are prepared. The terpene fraction, on the one hand, consisting principally of *d*-limonene, is characterized by strong dextrorotation, and affords a good yield of limonene tetrabromide. The sesquiterpene fraction, consisting principally of bisabolene, is lævogyrate and can be further characterized by the bisabolene trihydrochloride.

Böcker has tested his method in connection with a number of experimental mixtures and obtained good results. In connection with a terpene-free lemon oil produced by nimself, he obtained 51.5 p.c. of citral and 21 p.c. of hydrocarbons. In connection with a terpene- and sesquiterpene-free oil, also produced by himself, he found 62 p.c. of citral and traces of hydrocarbons too small in amount to be measured. In terpene-free lemon oils he regards a 25 to 30 p.c. hydrocarbon content as normal.

A comparison of the citral and hydrocarbon contents is said to enable the detection of the addition of lemongrass citral to a concentrated oil. Tests made with two oils, to which 20 p.c. of citral had been added, revealed that the exact amount of the addition could not be proven, but that only one-half thereof was indicated. Nevertheless, the minimum of adulteration can be recognized.

For the purpose of valuation, Böcker[1]) proceeds from the consideration that a lemon oil, freed entirely of its hydrocarbons, contains a maximum of 66 p.c. citral. This leads to the following table: --

Hydrocarbon content.	Highest admissible citral content.	Hydrocarbon content	Highest admissible citral content.
0 p.c.	. . 66 p.c.	30 p.c.	. . 46.2 p.c.
5 „	. . 62.7 „	35 „	. . 42.9 „
10 „	. . 59.4 „	40 „	. . 39.6 „
15 „	. . 56.1 „	45 „	. . 36.3 „
20 „	. . 52.8 „	50 „	. . 33 „
25 „	. . 49.5 „		

This table can be supplemented as desired, since for every 1 p.c. of hydrocarbon 0.66 p.c. citral should be deducted. Hence

[1]) Journ. f. prakt. Chem. II. 90 (1914), 393.

in passing judgment on an concentrated oil, the above table should be consulted to ascertain whether the hydrocarbon content agrees with the citral content. If the oil in question contains more *citral* than it should contain according to this table, this may be regarded as adulteration with added citral. In order to ascertain the minimum amount of added citral, the maximum citral content corresponding to the hydrocarbon content, as shown in the table, is noted. This amount of *natural citral* is deducted from the citral found by the sulphite assay. The difference stands for the minimum amount of citral added.

The details of the computation can be explained better with the aid of data supplied by Böcker. Having ascertained the presence of 15 p.c. of hydrocarbon and 61 p.c. of citral, the above table reveals that these values do not correspond, since according to Böcker the citral content of an oil containing 15 p.c. of hydrocarbon should not exceed 56 p.c. Hence citral from another source must have been added. Inasmuch as a normal with 56 p.c. citral should contain 100 - 56 = 44 p.c. of non-citral, and since the examined oil contains only 100 − 61 = 39 p.c. of non-citral, the normal citral content of the latter is revealed by the following equation: $44:56 = 39:x$; when $x = 49.63$. This number corresponds to the highest lemon oil citral content of an oil containing 39 p.c. of non-citral. Inasmuch, however, as 61 p.c. have been found, an adulteration with at least $61 - 49.63 = 11.37$ p.c. of foreign citral may be assumed.

Whether this method is of general application to all concentrated oils produced by different methods, can be ascertained only by experiment. It is noteworthy that, according to the method of production, other constituents than the hydrocarbons may be removed from the original oil. This may result in an increased citral content of the concentrated oil. Hence, a high citral content may not invariably indicate adulteration.

ADULTERANTS. Twenty-five years ago, when the constants of pure lemon oil were not known and when the polariscope was not utilized in its examination, French and American turpentine oil[1]) were the common adulterants, as revealed by

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[1]) More recently the strongly dextrogyrate Greek oil is being used for this purpose. E. J. Parry, Perfum. Record 2 (1911), 209.

the laboratory records of Schimmel & Co. This firm having
proceeded against the addition of turpentine oil by means of
the polariscope method, the adulterators took recourse to
mixtures of turpentine oil with carvene, orange oil terpenes, or
distilled lemon oil. Later, when the production of terpene-free
lemon oil came into vogue, the citrene resulting as waste product,
became the most favored and dangerous adulterant, for its detec-
tion, like that of citral from lemon grass oil, is exceedingly
difficult. Of adulterants that can be detected readily, the follo-
wing have been observed: — cedarwood oil, stearin[1]), mineral
oils[2]), alcohol[2]), castor oil[3]) and finally mixtures of alcohol and
glyceryl acetate[1]).

418. Lemon Petitgrain Oil.

As *petitgrain citronnier* an oil is designated which is
distilled from the twigs, leaves and unripe fruits of the lemon
tree[5]). Its odor resembles that of petit grain oil but the lemon-
like aroma betrays the origin of the oil. $d_{15°}$ 0.868 to 0.894;
$\alpha_0 + 14$ to $+35$; S. V. 14 to 46; aldehyde content 20 to 30 p.c.
Its constituents are: *camphene*[6]) (?), *limonene* (m. p. of tetra-
bromide 104°)[6]), *linalool*[6]) (?), *citral* (m. p. of citryl-β-napthocin-
chonic acid. m. p. 197°)[7])[6]) and *geraniol* (oxidation to citral)[6]).
The alcohols are present both free and as ester.

419. Oil of Sweet Orange.

**Oleum Aurantii dulcis. - - Süßes Pomeranzenschalenöl, Süßes Orangenschalenöl,
Apfelsinenschalenöl. — Essence d'Orange Portugal.**

Origin and Production. The mother plant of the sweet orange
is *Citrus Aurantium,* L. *(C. vulgaris,* Risso), subspec. *sinensis*

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[1]) G. Boswigi, Chemist and Druggist 55 (1899), 710.

[2]) Report of Schimmel & Co. April 1908, 45.

[3]) Parry, Chemist and Druggist 74 (1909), 121.

[4]) Report of Schimmel & Co. April 1913, 61.

[5]) Report of Schimmel & Co. October 1896, 62; April 1902, 79. — A. Hesse,
Chem. Zeitschr. 2 (1903), 465. — J. C. Umney and C. T. Bennett, Pharmaceutical
Journ. 75 (1905), 861. — Berichte von Roure-Bertrand Fils October 1904, 39. —
E. J. Parry, Perfum. Record 4 (1913), 280.

[6]) G. Litterer, Bull. Soc. chim. 33 (1905), 1081.

[7]) Schimmel & Co.. *loc. cit.*

(Gall.) *(C. Aurantium,* var. *dulce,* L., also in part, *C. Aurantium,* Risso). Like lemon oil, this oil is obtained by expression, both in Sicily and Calabria. In recent years occasional samples have reached Europe from the West Indies. Likewise, as with lemon, the attempt has been made in California to obtain a socalled "oleoresin" by means of extraction with volatile solvents. (Comp. under lemon oil, p. 14.)

Properties. Oil of sweet orange is a yellow to yellowish-brown liquid with a characteristic odor of oranges and a mild aromatic, not bitter taste. $d_{15°}$ 0.848 to 0.853; $\alpha_{D20°}$[1]) $+ 95°30'$ to $+ 98°$; $\alpha_{D20°}$ of the first 10 p.c. of fractional distillate not lower, or at most but slightly lower, than the α_D of the original oil (Comp. under lemon oil, p. 43); $n_{D20°}$ 1.473 to 1.475; decyl aldehyde content as determined after a two hours reaction with phenylhydrazine, 1.3 to 2.7 p.c. As a rule the oil does not form a clear solution with 90 p.c. alcohol (soluble in 7 to 8 vol.) because of its waxy, non-volatile constituents, some of which separate from the oil after long standing. The oil begins to boil at 175°. Up to 180° nine-tenths of the oil distil over.

The evaporation residue (See p. 68 under Bergamot oil) amounts to 1.5 to 4.2 p.c. A. V. of the residue 11 to 28; E. V. 118 to 157.

Rectified oil of orange is colorless. Its specific gravity is somewhat lower and its optical rotation somewhat higher than that of the original oil. The rectified oil has poor keeping qualities. It spoils rapidly, acquiring a stale, irritating odor.

The following constants were observed in connection with several oils from Jamaica[2]): $d_{15°}$ 0.8481 to 0.8491; $\alpha_{D20°}$ $+ 97°43'$ to $+ 98°2'$; α_D of the first 10 p.c. $+ 96°32'$ to $+ 97°30'$;

[1]) Like that of lemon oil, the angle of rotation of orange oil changes with differences in temperature, being reduced with increasing temperature. Hence, in order to obtain comparable data, it is necessary to record the exact temperature at which the observation was made and to recompute the angle of rotation for 20°. For every degree in temperature between $+$ 10 and $+ 20°$ the difference in the angle of rotation is 14.5 minutes, between $+ 20$ and $+ 30°$ it is 13.2 minutes. When recomputing for 20° it is necessary, therefore to deduct 14.5 minutes for every degree in temperature if the observation was made below 20° and to add 13.2 minutes for every degree in temperature if the observation was made above 20°.

[2]) Comp. p. 57.

n_{D20}. 1.46984 (1 determination); decylic aldehyde 2.3 to 3.8 p.c.; evaporation residue 1.4 to 2.0 p.c.

An oil from Dominica[1]) had the following constants: — d_{15}. 0.8486; α_{D20}. $+ 98°21'$; α_{D} of the first 10 p.c. $+ 97°40'$; evaporation residue 1.6 p.c., with S.V. 171.5.

In connection with three samples of oleoresin of orange the following constants were observed: — d_{15}. 0.8535 to 0.8723; α_{D20} about $+ 75$ to $+ 89°$ (an approximate determination only was possible because of the dark brown color of the preparation), α_{D} of the first 10 p.c. $|$ 90°54' to $+ 96°26'$, evaporation residue 11 to 14.7 p.c., A. V. of the residue 13.5, E. V. 107.0 to 112.0.

Properties of the terpenes from orange oil: d_{15}. 0.847 to 0.854; α_{D} $+ 95°50'$ to $+100°18'$; n_{D20}. about 1.473; soluble in 8 to 9.5 vol. of 90 p.c. alcohol, with partial turbidity.

Composition. As shown by Wallach[2]), oil of orange consists to the extent of at least 90 p.c. of d-*limonene* (m. p. of dihydro-chloride 50°[3]); m. p. of tetrabromide 104 to 105°[2]). Inasmuch as other hydrocarbons are entirely absent, the oil is well suited to the preparation of pure d-limonene. The absence of pinene is important as a factor in determining adulteration with turpentine oil.

Our knowledge of the oxygenated constituents we owe principally to K. Stephan[4]) who had 42 kg. of oil available for his investigation. By means of fractional distillation he obtained 530 g. of terpenefree constituents. With the aid of bisulphite he isolated an oil which had a uniform boiling point of 93 to 94° (12 mm.) and which was identified as n-*decylic* aldehyde by elementary analysis, oxidation to *n*-caprinic acid and by its naphthocinchoninic acid melting at 237°. Other aldehydes were not present. It is true that in 1891 F. W. Semmler[5]) found citral in oil of orange. However, it may be assumed that the oil examined by him was adulterated with lemon oil, since his

[1]) Examined in the laboratory of Schimmel & Co.

[2]) Liebig's Annalen **227** (1884), 289. Comp. also Völckel, *ibidem* **39** (1841), 120 and C. R. A. Wright and H. Piesse, Chem. News **24** (1871), 147; Chem. Zentralbl. 1871, 740.

[3]) E. Soubeiran and H. Capitaine, Liebig's Annalen **34** (1840), 319.

[4]) Journ. f. prakt. Chem. II. **62** (1900), 523. — Report of Schimmel & Co. October 1900, 28.

[5]) Berl. Berichte **24** (1891), 202.

investigation dates back to a time when it was impossible to determine the purity of orange oil by analytical means. Neither is it likely that citronellal is a constituent of unadulterated oil of orange. This H. Flatau and J. Labbé[1]) claim to have found, without, however, supplying any analytical proof.

In the terpene-free oil deprived of its aldehyde content, Stephan found the following alcohols: d-*linalool* (oxidation to citral; rearrangement, by means of formic acid, to *l*-terpineol melting at 35 to 36°); n-*nonylic alcohol* (nonylic aldehyde; m. p. of nonylic acid 15°) and *d*-terpineol (m. p. 38 to 40°; m. p. of terpineol nitrolpiperidide 154 to 155°; m. p. of terpinyl phenyl urethane 111 to 112°).

The occurrence of linalool (b. p. 199 to 200°; oxidation to citral) had previously been demonstrated by E. J. Parry[2]). The socalled myristicol ($C_{10}H_{16}O$), boiling between 212 to 218, found by Wright[3]), possibly consisted principally of terpineol.

Part of the alcohols exists in the oil in the form of esters combined with *n*-caprylic acid (m. p. 15°; b. p. 236 to 237°; analysis of the silver salt[4])).

The fluorescence which is shown more distinctly by the oil freed of its terpenes, was attributed by Parry[2]) to *anthranilic acid methyl ester*. Schimmel & Co.[5]) succeeded in proving the presence of this ester.

The composition of the non-volatile residue of oil of orange has not been revealed sufficiently. It is rather difficultly soluble in alcohol. If boiled with alcohol to remove admixtures, the insoluble portion melts at 67 to 68° and shows a S. V. of 65. From the saponification liquid a solid acid was separated which melted at 77 to 78 and the barium salt of which, upon analysis, gave values corresponding approximately with cerotinic acid, $C_{26}H_{52}O_2$. From the same saponification liquid, ether extracted an oil which solidified and which, upon re-crystallization melted at 138. The elementary analysis of this substance yielded results

[1]) Bull. Soc. chim. III. 19 (1898), 361.

[2]) Chemist and Druggist 56 (1900), 462 u. 722.

[3]) Chem. News 27 (1873), 82; Chem. Zentralbl. 1873, 260. — Berl. Berichte 6 (1873), 148.

[4]) Stephan, *loc. cit.*

[5]) Report of Schimmel & Co. April 1900, 21.

corresponding fairly with $C_{28}H_{48}O_2$. Dissolved in chloroform it, yielded the Liebermann cholesterol reaction[1]).

Examination. The physical constants of orange oil vary within narrow limits. On account of its low specific gravity and exceedingly high angle of rotation, it is an easy matter to detect without doubt the addition of foreign substances. There appears to be no adulterant that does not affect one of these two properties.

For the detection of turpentine oil the lowest boiling fraction of the oil is fractionated repeatedly with the aid of a dephlegmator. Boiling point and optical rotation reveal the presence of pinene. If this is not sufficient, the pinene is converted into its nitrosochloride and this into either the nitrolbenzylamine or nitrolpiperidine base.

The decylic aldehyde content can readily be determined by means of phenylhydrazine. The method to be employed is the same as that used for the citral assay in lemon oil (Comp. p. 41) with this difference that the mixture of orange oil and phenyl-hydrazine solution should be allowed to stand for 2 hours. Decylic aldehyde reacts slower than does citral so that complete reaction is not assumed within less time. With mixtures of decylic aldehyde of known content, Schimmel & Co. have obtained very satisfactory results in this manner. Poorer results are, in turn, obtained by prolonging the reaction time beyond the two hours. According to observations made thus for, the decylic aldehyde content of oil of orange varies between 1.3 and 2.7 p.c.

420. Oil of Bitter Orange.

Oleum Auranti amari. — Bitteres Pomeranzenschalenöl. —
Essence d'Orange Bigarade.

Origin. Compared with sweet orange oil, that of the bitter orange, *Citrus Aurantium,* L., subspec. *amara,* L. (*C. Bigaradia,* Risso), plays but an unimportant role. Like the former it is produced in Sicily and southern Calabria in the same manner.

Properties. The principal difference between the bitter and sweet orange oil lies in the bitter taste of the former and in

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[1]) Berl. Berichte 18 (1885), 1804.

the lower angle of rotation. d_{16}. 0.852 to 0.857, usually 0.854 to 0.856; α_{D20°. $+89$ to $+94^\circ$ (rarely $+88^\circ$); α_D of the first 10 p.c. higher than the α_D of the original oil; n_{D20°. 1.473 to 1.475. The decylic aldehyde content about 1 p.c. (after interaction for 2 hours with phenylhydrazine). Soluble in 7 to 8 vol. of 90 p.c. alcohol, the rotation being turbid. The evaporation residue varies between 3 and 5 p.c. As to the A. V. and E. V. of this residue sufficient observations are not available, but these do not appear to differ from those determined for the sweet oil.

Constants of oils of special origin.

a) expressed oils.

Geographical origin	d_{16}	α_{D20°	α_D of the first 10 p.c.	evaporation residue
Spain[4]	0.855	$+95^\circ 55'$	—	—
South America[1] . .	0.8542	$-95^\circ 56'$	$+96^\circ 44'$	4.0 p.c.
Jamaica[2]	0.8517	$+96^\circ 20'$	$+96\ 40'$	2.6 p.c.
„ [2]	0.8521	$+96^\circ 58'$	$+95^\circ 53'$	3.2 p.c.
„ [1]	0.8537	$+92^\circ 57'$	$+92\ 20'$	3 p.c.
„ [1]	0.8527	$+96^\circ 2'$	$+95\ 50'$	3 p.c.

b) distilled oils.

	d_{16}	α_{D20°		
Amani[1][3]	0.8481	$+97\ 38'$		—
West Indies[4]				
from mature oranges	0.8482	$+91\ 24'$		
„ immature „	0.8485	$+94\ 30'$	-	—
„ „ „	0.8490	$+90\ 22'$	—	—
„ whole „	0.8481	$+97^\circ 30'$	—	—
„ orange peels	0.8500	$+89\ 4'$	—	
Seychelles[5]				
from immature fruits	0.856	$+85\ 33'$	—	—
„ mature „	0.862	$+84\ 32'$	.	—

Composition. No work on the composition of bitter orange oil has yet been published. On account of the great similarity

[1] Observation made in the laboratory of Schimmel & Co.

[2] Report of Schimmel & Co. October 1909, 66.

[3] Yield 1.4 p.c. of the peels. Comp. Der Pflanzer 2 (1906), 176; Report of Schimmel & Co. April 1907, 52.

[4] Report of Schimmel & Co. April 1910, 68.

[5] *Ibidem* October 1906, 65.

of the two oils, its composition may be assumed to be very much like that of the sweet oil. The substance which imparts the bitter taste to the oil presumably is to be sought for in the evaporation residue.

421. Oil of Bergamot.

Oleum Bergamottae. -- Bergamottöl. - Essence de Bergamote.

Origin and Production. The bergamot tree, *Citrus Aurantium*, L. (*C. vulgaris*, Risso) subspec. *Bergamia* (Risso et Poiteau) Wight et Arn. (*C. Bergamia*, Risso) is cultivated exclusively in Calabria, the fruit being used for oil production only. In Sicily the tree does not prosper. Its geographic distribution is indicated on the accompanying chart (p. 6).

On account of the regular spherical shape of the bergamot fruit it would seem to lend itself for the mechanical production of the oil. Hence, suggestions for apparatus for this purpose have not been wanting[1]). For some time the *macchina* (fig. 10), a primitive apparatus run by hand, has been used.

The wooden frame *A* supports a wooden wheel *6*, which revolves on its horizontal axis, and on the inner-side of which 36 wooden plugs are inserted. These clutch a driving-gear which turns on its vertical axis *3*. When the wheel *6* is turned by hand, this* driving-gear rotates three times as fast. The axis *3* can be raised or lowered in its supports. The lower portion of the revolving mechanism is supplied with a disc *4* mounted on a zinc cylinder. A similar disc, *5*, is mounted in the lower box of the *macchina*. The disc *5* is perforated so that the exuding oil may flow into a vessel placed underneath.

The *macchina* is operated in the following manner. First of all the two discs are separated by pressing down the two-armed lever *1*, which turns on its pivots *9* and *10*, and is secured by means of the bar *2*. The fruits are then introduced between the two discs, the lower one of which is stationary. The bar *2* is then removed so that the entire weight of the driving gear rests on the fruits. When the drive wheel *6* is turned, the fruits

[1]) Compare by way of illustration W. A. D. Allport and T. J. W. C. Davenport, Roseau, Dominica, B. W. I. U. S. Pat. 1002020, Aug. 29, 1911. Journ. Soc. chem. Ind. 30 (1911), 1138.

between the discs acquire a rotary motion. The discs, being provided with either points or knives (see below), rupture the
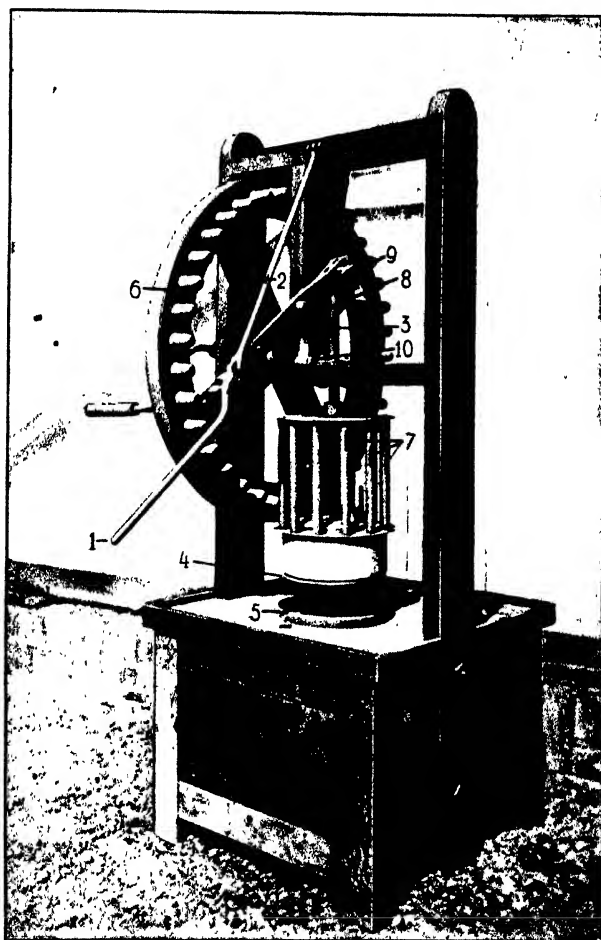
Fig. 10. *Macchina* for the production of bergamot oil.

oil cells, the contents of which empty into the container placed underneath the lower disc. The drive wheel 6 is turned until a bell rings which is operated by the wheel 8. This occurs

after the wheel 6 has been revolved 36 times and the driving
gear and upper disc 108 times.

Two kinds of discs are employed. The one consists of flat
zinc plates provided with pyramidal points, the lower of the two
plates having four narrow openings near the margin for the
removal of the oil (fig. 11). The other kind consists of somewhat
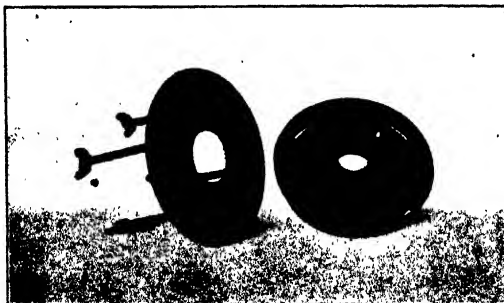
Fig. 11.
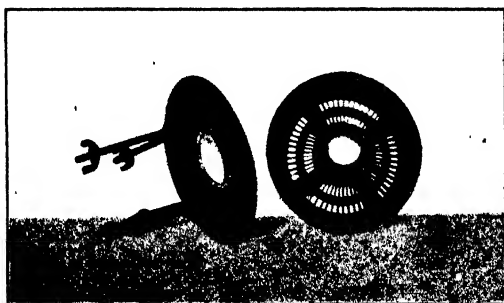
Fig. 12.

hemispherical plates of zinc, the inner surface of which are
provided with brass knife blades inserted at a certain angle.
The lower of these has a number of openings (fig. 12).

In Calabria lemons are also expressed with the aid of this
machine. However, the oil thus obtained is invariably green
(see Properties on p. 20) and is not saleable as such. It is said
to be used exclusively for the adulteration of bergamot oil.

Properties. Oil of bergamot is a brownish-yellow or honey-colored liquid, but frequently green because of a copper content[1]. It has a bitter taste and a very pleasant odor. d_{15} 0.881 to 0.886, in very rare instances 0.888; $\alpha_D + 8$ to $+ 22°$, in certain oils, however, optical rotations as low as $+ 5° 24'$ and as high as $+ 24°$ have been observed[2]; $n_{D20°}$ 1.464 to 1.468; A. V. 1 to 3.5[3]).

The linalyl acetate content, which determines the value of the oil, is as a rule 34 to 40 p.c., rarely 45 p.c. At the beginning of the season, when fruits not quite ripe are used, oils are occasionally obtained with a lower ester content (down to 30 p.c.). With the increasing maturity of the fruit the ester content increases[4].

Of 90 p.c. alcohol 1 vol. is requisite to effect solution. When more alcohol is added, the solution remains clear in most instances and but rarely produces slight turbidity. Some oils dissolve in 1 to 2 vol. of 80 p.c. alcohol, but as a rule the solution becomes turbid upon the addition of more solvent[5].

The evaporation residue (for method see under Examination on p. 68) as a rule amounts to from 4.5 to 6 p.c., but occasionally is as low as 4 p.c. A. V. of the evaporation residue 19 to 30; E. V. (after first decoloration! See under Examination on p. 74) 117 to 173.

It may be of interest to add that two bergamot oils, which had been obtained from Ischia and from the vicinity of Palermo, hence from districts in which this oil had not previously been produced, revealed no differences in their properties from the normal standards.

The oil from the island of Ischia[6]) was brownish-green in color, had a strong characteristic odor and revealed the following

[1]) Bericht von Schimmel & Co. April 1889, 16.

[2]) Report of Schimmel & Co. April 1910, 59.

[3]) *Ibidem* April 1908, 40.

[4]) According to A. Bornträger (Zeitschr. f. anal. Chem. 35 [1896], 35; Chem. Zentralbl. 1896, I. 514) the evaporation residue yields saponification values corresponding to 2 p.c. of linalyl acetate. To be exact this number should be deducted from the percentage of ester found upon saponification of the oil. However, no cognisance is taken of this fact for it would complicate the method unnecessarily.

[5]) Report of Schimmel & Co. April 1909, 50, footnote 1.

[6]) *Ibidem* April 1908, 40.

constants: $-d_{15}$ 0.8828; $\alpha_D + 13'$; A. V. 1.8; E. V. 96,4, corresponding to 33.7 p.c. of linalyl acetate; evaporation residue 5.2 p.c.; soluble in 0.3 vol. and more of 90 p.c. alcohol.

The examination of the oil from Palermo revealed the following constants[1]: d_{15} 0.8829; $\alpha_D + 15°\,20'$; A. V. 1.5; E. V. 100.7 corresponding to 35.2 p.c. of linalyl acetate; evaporation residue 5.8 p.c.; soluble in 0.5 vol. and more of 90 p.c. alcohol, with 80 p.c. alcohol a clear solution could not be obtained.

Rectified bergamot oil is colorless and has a lower specific gravity (0.865 to 0.875) also a somewhat higher angle of rotation than the original oil. As a rule the rectified oil is inferior, since the steam distillation causes the partial decomposition of the esters.

Oils expressed from immature fruits that have fallen from the trees or that have been blown down by storm are admixed at times with the normal oil. Such oils have been examined by G. H. Ogston and Moore[2]. Their specific gravity varied between 0.8789 and 0.8833; their α_D between $+7$ and $+18.6$ and their ester content between 26.7 and 33.5 p.c.

Nero di bergamotto, i. e. essence of black bergamot are terms which, according to Ogston and Moore[2], are applied to an oil obtained from the rinds of an immature hybrid fruit. According to Bertè and Romeo[3], however, the term is applied to an oil expressed from unripe fallen fruits *(Bergamottella)*. It is occasionally used as adulterant of bergamot oil. It is dark in color, has a rather high specific gravity (0.890 to 0.898) and a low ester content (20 to 35 p.c.).

From the residues of separation *(feccie di bergamotto)*[3], and filtration, also from the expressed rinds, an oil is occasionally obtained by distillation. This is also added to the normal bergamot oil. It is colorless or yellowish; d_{15} about 0.865; α_D (determined for one sample) $+24°\,39'$; ester content 3 to 6 p.c.

Composition. As early as 1840 E. Soubeiran and H. Capitaine[1] pointed to the presence of more than one terpene. In 1884

[1]) Report of Schimmel & Co. April 1910, 58.

[2]) Chemist and Druggist 60 (1902), 154.

[3]) E. Bertè and G. Romeo, *Annali del laboratorio chimico della camera di commercio ed arti della provincia di Messina.* Messina 1908; Report of Schimmel & Co. April 1909, 50.

[1]) Liebig's Annalen 35 (1840), 313.

O. Wallach[1]) showed that fraction 175 to 180 contains *limonene*
(*d*-limonene). Fraction 180 to 190 added bromine but did not
yield a crystalline bromide. When heating this fraction to a
higher temperature, high-boiling condensation products resulted,
and refractionation yielded a fraction up to 190° which formed
dipentene tetrabromide melting at 124 to 125. This mode of
procedure does not reveal whether the dipentene was contained
in the original oil or was formed by heating the fraction 180
to 190° unquestionably containing some linalool. Neither can
the observation of F. W. Semmler and F. Tiemann[2]), who found
that the fraction boiling 17° higher than the limonene fraction
yielded dipentene tetrabromide, be regarded as a proof of the
occurrence of dipentene in bergamot oil.

Our knowledge of the important odoriferous constituents of
bergamot oil we owe to well-nigh simultaneous publications by
Semmler and Tiemann[2]) on the one hand and by J. Bertram and
H. Walbaum[3]) on the other hand. These revealed that the principal
bearer of the odor of bergamot oil is the *acetic ester* (analysis
of the Ag-salt)[3]) of l-*linalool* (oxidation to citral)[2]), namely to
l-*linalyl acetate*.

Likewise of some importance in this connection is the free
l-linalool, possibly also small amounts of other substances not
yet isolated.

According to F. Elze[4]), three other alcohols are contained
in bergamot oil. He examined a fraction which, on a factory
scale, was obtained to the extent of 25 p.c. in the production
of terpene-free bergamot oil. After saponification, distillation
with water vapor, and fractionation, it yielded an oil with the
following properties: d_{15} 0.890; $\alpha - 10'$ (in a 100 mm. tube).
Treated with phthalic acid anhydride, a small amount of an oil
was obtained which proved to be *dihydrocuminic alcohol* (m. p.
of naphthyl urethane 146 to 147) and which upon oxidation
with Beckmann's chromic acid mixture yielded an aldehyde
boiling at 235° that had a cumin-like odor. Regenerated from
its semicarbazone (m.p. 198 to 199°) d_{15} was 0.970 and α_0 39°.

¹) Liebig's Annalen 227 (1884), 290.
²) Berl. Berichte 25 (1892), 1182. •
³) Journ. f. prakt. Chem. II. 45 (1892), 602.
⁴) Chem. Ztg. 34 (1910), 538.

The bulk of the alcohol mixture, however, consisted of *nerol* (d_{15} 0.880) which was further characterized by its tetrabromide, melting at 118°, and its diphenyl urethane, melting at 50°.

In that portion which did not react with phthalic acid anhydride, Elze proved the presence of the *terpineol* melting at 35° (m. p. of the phenylurethane 110°). This observation is very important since it has been found recently that bergamot oil is occassionally adulterated with terpinyl acetate[1]). Hence it is a mooted question at present whether terpineol is a normal constituent or not.

Quite odorless is the *bergaptene* which occurs in the oil to the extent of 5 p.c. A series of contributions has been published on this subject[2]). According to Pomeranz[3]), bergaptene, $C_{12}H_8O_4$, consists of fine, white needles with a silky lustre. They are tasteless and at ordinary temperature odorless. However, when heated they develop vapors with an aromatic odor and melt at 188°. Bergaptene is the monomethyl ether of a dihydroxycumarin derivable from phloroglucinol. When treated with methyl iodide and alcoholic potassium hydroxide, methylbergaptenic acid and its methyl ester result. Hence bergaptene is the inner anhydride of bergaptenic acid. H. Thoms and E. Baetcke[4]) assign to it the following formula: —
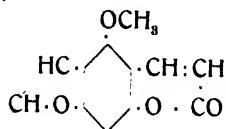
It is isomeric with xanthotoxin (comp. vol. II, p. 632).

Several other constituents have been found in a bergamot oil by H. E. Burgess and T. H. Page[5]). Although these investigators

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[1]) Report of Schimmel & Co. April 1910, 60.

[2]) G. J. Mulder, Liebig's Annalen 31 (1839), 70. — C. Ohme, *ibidem* 31 (1839), 320. — Franke, Dissertation. Erlangen 1880. — R. Godeffroy, Zeitschr. d. allgem. österr. Apoth.-Ver. 19 (1881), 1; Chem. Zentralbl. 1881, 372. — W. A. Tilden and C. R. Beck, Journ. chem. Soc. 57 (1890), 323; Chem. Zentralbl. 1890, I. 719. — L. Crismer, Bull. Soc. chim. III. 6 (1891), 30; Chem. Zentralbl. 1891, II. 379.

[3]) Monatsh. f. Chem. 12 (1891), 379 and 14 (1893), 28.

[4]) Berl. Berichte 45 (1912), 3705.

[5]) Journ. chem. Soc. 85 (1904), 1327.

contend that the oil examined by them was pure, this does not follow from the constants recorded (*viz.* d_{15} 0.885; $[\alpha]_D + 8°$; n_{D20} 1.4648; ester content not mentioned). Hence the examination will have to be repeated with material of unquestioned purity, before octylene, pinene, camphene and bisabolene can be regarded as constituents of bergamot oil. In the lowest fractions *acetic acid* (analysis of Ba-salt) was found. It was scarcely necessary to prove the presence of free acetic acid, since it is a well-known fact that the acids, which in the volatile oils are combined with alcohols, also occur in the free state to a slight extent. Moreover, Burgess and Page did not prove the presence of free acetic acid in bergamot oil, for they accumulated it by means of fractionation of the oil, a process by which the acid is formed from the linalyl acetate, as they themselves surmise.

Fraction 150 to 155° revealed a very low specific gravity and a low refractive index. Hence they infer the presence of an olefinic hydrocarbon, octylene. This inference Burgess and Page endeavor to substantiate by pointing out that the odor of this fraction reminds of the octylene found by the same authors in lemon oil, also by demonstrating that upon oxidation with potassium permanganate butyric acid (identified only by its odor) results.

Lævogyrate ($[\alpha]_D - 8.3$) *α-pinene* and lævogyrate ($[\alpha]_D - 22.8°$) *camphene* were identified in fractions 157 to 158 and 164 to 165° respectively. The former was characterized by its hydrochloride (m. p 125°), the latter by its conversion into *iso*borneol (m. p. 203°). The higher boiling fraction of the bergamot oil contained *bisabolene* (limene) $C_{15}H_{24}$ (m. p. of hydrochloride 79°).

The formation of the individual constituents and the changes which they undergo in the plant have been subjected to an investigation by E. Charabot[1]. For this purpose two oils were examined: one had been prepared from fully developed but green fruit, the other from ripe fruits picked from the same trees. The results are herewith tabulated: —

[1] Compt. rend. 129 (1899), 728.

	Oil from immature fruits.	Oil from mature fruits.
$d_{14°}$	0.882	0.883
α_D	$+14°38'$	$+20°30'$
Free acids	0.289 p.c.	0.283 p.c.
(computed as acetic acid)		
Linalyl acetate	33.8 p.c.	37.3 p.c.
Free linalool[1])	13.9 p.c.	5.9 p.c.
Total linalool	40.5 p.c.	35.5 p.c.

From the above data it becomes apparent that the ester content has increased during the ripening of the fruit, whereas the amounts of free and total linalool have both decreased. This observation agrees with practical experiences, for the producers of bergamot oil have known that the oil from ripe fruits is better and richer in ester than the oil obtained early in the campaign from not fully matured material.

In order to ascertain the terpene content of both oils, they were saponified and then fractionated with the following results:

160 ccm. of the oil from the immature fruits: —

93 ccm. b. p. 177 to 183°; $\alpha_D + 34°10'$; d 0.887
36 „ „ 183 „ 200°; $\alpha_D + 2°14'$; d —

160 ccm. of the oil from the mature fruits: —

105 ccm. b. p. 177 to 183°; $\alpha_D + 34°$ d 0.885
30 „ „ 183 „ 200°; $\alpha_D + 4°$ d —

Hence the terpene content of the bergamot oil increased with the ripening of the fruit, but the ratio between limonene and dipentene[2]) remained the same, as was demonstrated by other experiments. From these data Charabot draws the following conclusions: — Linalool results in the fruit previous to the ester.

[1]) That an approximate assay of linalool in the oil diluted with xylene can be made was not known at the time. The amount of free linalool was obtained by difference of the ester content of the original oil and the acetylated oil. Inasmuch as the conditions of the assays are the same throughout, the results are comparable.

[2]) As already stated it has not yet been proven positively that dipentene occurs in oil of bergamot.

During the process of ripening a part of the linalool is converted into linalylacetate by means of the free ácetic acid, another part is dehydrated to terpenes.

Although there appears no reason for questioning the correctness of this proof, it would be desirable, nevertheless, to ascertain by repetition of the experiment whether the data have general bearing or not.

Examination. Formerly it was not a difficult matter to ascertain the purity of bergamot oil, for the adulterants used greatly altered the physical constants. Inasmuch as the specific gravity of the oil fluctuates within the narrow limits of 0.881 and 0.886, the addition of turpentine oil[1]), lemon oil, orange oil and of distilled bergamot oil produced a lowering of the density, that of fatty oils, cedarwood oil or gurjun balsam oil an increase in density. Some of these adulterants also alter the angle of rotation ($+ 8$ to $+ 20°$) of the pure oil.

Nevertheless, in spite of the normal rotation, an oil might be adulterated provided the normal limits were not interfered with by the proper selection of adulterants such as turpentine oil with lemon oil or orange oil. In order to detect such adulteration R. Romeo and G. Moricca[2]) fractionate 30 ccm. of bergamot oil into fractions of 5 ccm. and determine the angle of rotation of the first two fractions. In the case of pure oils, the rotation of the first fraction is greater than that of the second; in the case of adulteration, the reverse holds true.

The determination of the solubility in 90 p.c. alcohol affords but little guaranty of purity, for it enables the detection of gross adulteration only. As already pointed out, only some of the pure bergamot oils are soluble in 80 p.c. alcohol. If a given oil form a clear solution with this solvent, it may be regarded as free from fatty oils, turpentine oil and orange oil. If it does not form a clear solution, this may be due to an adulterant, such

[1]) It is probable that pinene is not a normal constituent of bergamot oil (see under Composition). The detection of pinene is, therefore, to be regarded as a proof of the presence of turpentine oil.

[2]) *Sull' analisi della essenza di bergamotto.* Messina 1905; Report of Schimmel & Co. October 1905, 26.

as fatty oil, or to larger amounts of bergaptene or waxy constituents.

DETERMINATION OF THE EVAPORATION RESIDUE. The proof of the presence of fatty oils or of difficultly volatile adulterants is brought by weighing the residue left upon evaporation at 100°. In the case of normal oils this amounts to from 4.5 to 6 p.c.

In order to carry out this test about 5 g. of oil are weighed accurately to the centigram in a tared glass, porcelain, or, better still, a metal dish, which is heated on a water bath until of constant weight and until the residue has lost every trace of odor of bergamot oil. This requires from 4 to 5 hrs. After cooling, the dish with residue is again weighed. If the residue amounts to more than 6 p.c. of the oil used, an inadmissible addition may be regarded as established. In the case of oils adulterated with turpentine oil, oil of orange, or distilled bergamot oil, the residue may be appreciably less than 4.5 or even less than 4 p.c. (comp. p. 61).

The esters which come into consideration as adulterants may best be considered in two groups:

Esters with readily volatile acids (terpinyl acetate and glyceryl acetate) and *esters with difficultly volatile acids* (esters of succinic, oxalic, tartaric, and citric acids).

DETECTION OF TERPINYL ACETATE. In a series of experiments made by Schimmel & Co.[1] it has been demonstrated that pure linalyl acetate is nearly fully saponified with $\frac{N}{2}$ alcoholic potassium hydroxide when heated for 1 hour on a water bath, whereas pure terpinyl acetate is only partly saponified in this time. Hence the ester value will increase upon prolonged saponification.

These results have been collected in the following table:—

Duration of saponification:		5 min.	15 min.	30 min.	45 min.	1 hr.	2 hrs.
Linalyl acetate Schimmel & Co.	E. V.	191.5	217.5	221.2	223.7	223.1	224.7
Terpinyl acetate	„	108.2	166.8	200.7	233.4	245.8	262.7
Bergamot oil	„	80.3	94.5	97.3	97.5	97.8	98.5
+ 5 p.c. terpinyl acetate	„	82.5	94.8	101.2	102.1	104.7	107.2
+ 10 p.c. „	„	79.9	96.4	102.8	105.2	108.8	112.5
+ 25 p.c. „	„	78.8	100.6	108.1	116.4	119.0	126.8

[1] Report of Schimmel & Co. October 1910, 60.

Still greater are the differences when one operates with dilute solutions for the shorter saponification period and with a large excess of alkali for the longer period. After numerous experiments Schimmel & Co.[1] have prepared the following directions for this *fractional saponification* method:

Four separate experiments are made. About 2 ccm. of oil are accurately weighed in each case, dissolved in about 5 ccm. of alcohol and a few drops of alcoholic phenolphthalein solution (1:100) added. The acid value is first determined with $\frac{N}{2}$ potassium hydroxide. To each of two of the flasks 10 ccm. of $\frac{N}{2}$ potassium hydroxide are added and the contents heated on the water bath for an hour in order to effect saponification in the well known manner. The contents of the third flask are boiled with 20 ccm. of the alkali for two hours and that of the fourth flask diluted with 25 ccm. neutral 96 p. c. alcohol and saponified for one hour with 10 ccm. of the standard alkali. For oils with a high percentage ester content 30 and 15 ccm. respectively of the standard alkali are used, and in the case of artificial esters as much as 40 and 20 ccm. respectively for the third and fourth flasks. At the close of the boiling, the flasks are quickly and unitormly cooled by placing them in cold water and the contents are titrated immediately.

In the case of bergamot and lavender oils the difference in the ester values, obtained by boiling for two hours and with the dilute solution for one hour, amounted to 3 or at most 4, whereas the ester values for the two normal determinations represented the approximate mean of these extremes. If terpinyl acetate be added, this difference increases. Moreover, the ester value obtained for the two-hour saponification increases in the ratio in which the terpinyl acetate is added, whereas that obtained for the oil diluted with alcohol increases but little. The ester values of the two normal saponifications invariably are in the mean. In the following table the data have been compiled that have been found for a pure bergamot oil and also for the same oil to which terpinyl acetate had been added in the proportions indicated.

[1] Report of Schimmel & Co. October 1911, 116.

Seminormal potassium hydroxide:	10 ccm.	20 ccm.	10 ccm. + 25 ccm. alc.	Difference between columns 2 and 3.
Duration of saponification:	1 hr.	2 hrs.	1 hr.	
Bergamot oil, pure	99.7	100.5	97.4	3.1
2 p.c. terpinyl acetate	102.1	104.5	98.1	6.4
4 „ „	103.3	108.1	98.1	10.0
6 „ „	105.7	112.2	98.6	13.6
8 „ „	107.0	114.4	98.4	16.0
10 „ „	108.6	118.1	99.1	19.0
15 „ „	113.4	126.7	101.0	25.7
20 „ „	118.0	135.6	101.3	34.3

Hence an addition of 10 p.c. terpinyl acetate produces a difference of 19 in the ester values. (In the case of normal saponification for one-half and one hour duration respectively, the difference is but 5.5; comp. the table on p. 73.) Inasmuch as the addition of but 2 p.c. of ester produces a difference of 6.4, the presence of even small amounts of adulteration can possibly be detected in this manner.

DETECTION OF GLYCERIN ACETATE. The detection of glycerin acetate, the use of which as adulterant was first pointed out by P. Jeancard and C. Satie[1]) and later by Heine & Co.[2]), depends on the relatively ready solubility of these esters in water. If a bergamot oil adulterated with these esters is shaken in a suitable manner with water, a certain percentage of these esters goes into solution. By means of subsequent saponification of this aqueous solution with potassium hydroxide the approximate ester content of the solution can be computed from the amount of alkali consumed.

According to Schimmel & Co.[3]) the determination is carried out in the following manner: 10 ccm. bergamot oil contained in a separating funnel are thoroughly shaken with 20 ccm. of 5 p.c. alcohol. After separation of the liquids, 10 ccm. of the filtered aqueous layer are neutralized with alkali and then saponified with 5 ccm. of $\frac{N}{2}$ potassium hydroxide for 1 hour on a water

[1]) Bull. Soc. chim. IV. 3 (1908), 155.
[2]) Seifensieder Ztg. 37 (1910), 750.
[3]) Report of Schimmel & Co. October 1910, 61 and April 1911, 151.

bath. For the saponification of these 10 ccm., pure bergamot oil required

0.08 ccm. semi-normal potassium hydroxide = 2.2 mg. KOH consumed
After the addition of

1 p.c. glycerin triacetate 0.58 ccm. –	16.2 „	„ were consumed
2½ „ „ „ 1.43 „	40.0 „	„ „ „
5 „ „ „ 2.79 „ ÷	78.0 „	„ „ „

1 g. glycerin monoacetate = 1.46 g. linalyl acetate
1 „ „ diacetate = 2.23 „ „ „
1 „ „ triacetate = 2.70 „ „ „

Hence the addition of 1 p.c. of glycerin acetate increases the consumption of alkali by about 15 mg.

DETECTION OF ESTERS THE ACIDS OF WHICH ARE DIFFICULTLY VOLATILE WITH WATER VAPOR. The method of determination worked out by Schimmel & Co.[1] is based on the exceedingly slight volatility with water vapor of the acids contained in these esters. Experiments with pure bergamot oil have shown that the natural acids, which have united with the alkali during the process of saponification can be distilled off almost entirely with water vapor after the addition of sulphuric acid. Hence the saponification of a pure bergamot oil requires but little more alkali than is required for the neutralization of the acids distilled over. For the purpose of this determination both acid and ester values of from 1.5 to 2 g. of oil are determined in the usual manner. After the addition of a few drops of $\frac{N}{2}$ potassium hydroxide solution, the contents of the saponification flask are evaporated to dryness. The residue is dissolved in about 5 ccm. of water, and the solution acidulated with 2 ccm. of dilute sulphuric acid. By means of the apparatus illustrated in fig. 13, steam is generated in flask a, passed through b and the condensed distillate collected in c. The distillation is conducted in such a manner that the contents of the saponification flask b are kept at about 10 ccm. by means of a small flame and that 250 ccm. of distillate are collected within half an hour. Subsequently another 100 ccm. are driven over. After the addition of a few drops of phenolphthalein solution the distillate is titrated with $\frac{N}{2}$ potassium hydroxide, or, for the sake of greater

[1] Report of Schimmel & Co. October 1910, 61.

accuracy, with $\frac{N}{10}$ alkali until the red color of the indicator
becomes permanent. The first 250 ccm. contain practically all
of the volatile acid, since the following 100 ccm. always require
but 0.1 to 0.2 ccm. of $\frac{N}{10}$ alkali. From the amount of alkali
consumed by the total distillate the *acid value II* for the
amount of oil taken is calculated. The difference between the
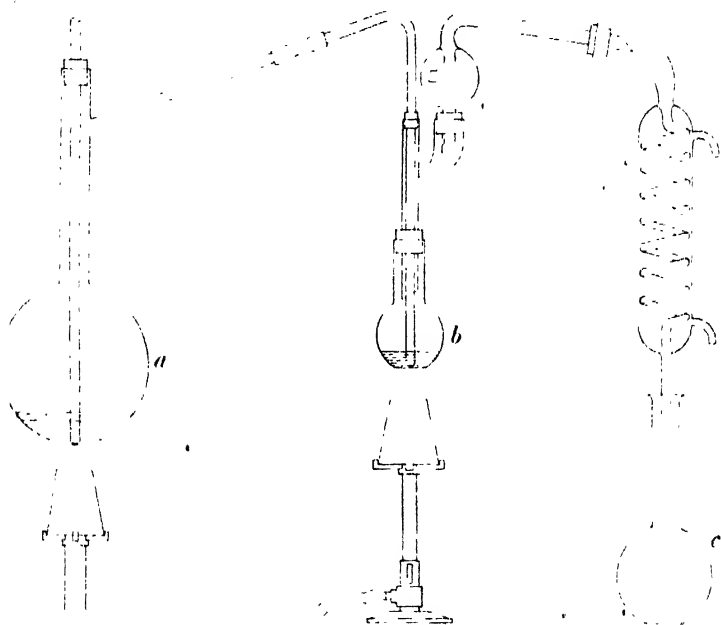saponification value of several pure oils and the acid value II

Fig. 13.

thus determined varied from 5 to 10[1]) (See Nos. 1 to 8 of the
accompanying table). Hence oils with a greater difference should
be regarded as either questionable or adulterated.

The differences in the acid values of the pure esters
(Nos. 9 to 11 of the accompanying table) vary from 596.4 to
745.8. Hence the addition of these esters to bergamot oil must

[1]) Report of Schimmel & Co., April 1911, 150.

correspondingly increase the differences between both values of oil thus adulterated (Nos. 12 to 20).

As shown by Nos. 21 and 22, adulteration with glycerin triacetate or terpinyl acetate cannot be detected by the distillation of the acids, since in these instances the differences lie within the limits for normal oils.

		A.V.	E.V. of the oil	S.V.	A.V. II of the oil	Diff.
No. 1	Bergamot oil 1.6		88.7	90.3	84.3	6.0
„ 2	„ 1.6		90.2	91.8	86.6	5.2
„ 3	„ 2.0		101.1	103.1	97.0	6.1
„ 4	„ 2.3		112.3	114.6	107.7	6.9
„ 5	„ 2.4		100.0	102.4	95.7	6.7
„ 6	„ 2.3		96.1	98.4	91.8	6.6
„ 7	„ 2.1		98.3	100.4	95.1	5.3
„ 8	„ 2.0		98.2	100.2	90.8	9.4
„ 9	Succinic acid diethyl ester .			638.4	7.3	631.1
„ 10	Citric acid triethyl ester . . 0.8		602.6	603.4	7.0	596.4
„ 11	Oxalic acid diethyl ester . .			753.0	7.2	745.8
	Bergamot oil after the addition of:					
„ 12	1 p.c. Succinic acid diethyl ester 2.1		103.5	105.6	94.1	11.5
„ 13	2 „ „ „ „ „ 2.1		109.9	112.0	93.1	18.9
„ 14	3 „ „ „ „ „ 2.1		116.2	118.3	92.8	25.5
„ 15	4 „ „ „ „ „ 2.1		121.7	123.8	91.8	32.0
„ 16	5 „ „ „ „ „ 2.1		127.6	129.7 •	91.5	38.2
„ 17	1 „ Citric acid triethyl ester 2.1		103.4	105.5	94.1	11.4
„ 18	2 „ „ „ „ „ 2.1		109.1	111.2	92.8	18.4
„ 19	1 „ Oxalic acid diethyl ester --			106.6	94.7	11.9
„ 20	2 „ „ „ „ „ —			113.3	92.5	20.8
„ 21	2 „ Glycerin triacetate . 2.1		111.2	113.3	108.7	4.6
„ 22	4 „ Terpinyl acetate . . . 2.4		103.2	105.6	100.0	5.6

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DETECTION OF CITRIC ACID ESTERS. If the residue of an oil is found too high, adulteration with fatty oil is no longer the only explanation, for in recent years citric acid triethyl ester (triethyl citrate[1])) must likewise be considered. The latter is a particularly serious adulteration since the addition of but small amounts materially increases the apparent ester content of the oil.

[1]) O. Wiegand and K. Rübke, Verfälschung von Bergamottöl mit Citronensäureester. Zeitschr. f. angew. Chem. 23 (1910), 1018. — Report of Schimmel & Co. October 1910, 59.

If a given oil is suspicious because of its high evaporation residue, this is transferred quantitatively to a saponification flask with the aid of alcohol and saponified in the usual manner with $\frac{N}{2}$ potassium hydroxide. The excess of alkali is titrated back with $\frac{N}{2}$ sulphuric acid, phenolphthalein being used as indicator. The *first decoloration* of the indicator is taken to indicate the end of the reaction, for subsequent reappearances of the red color may be due to the liberation of alkali by transformation of bergaptenic acid into bergaptene. The reappearance of the red color can be avoided in part by not diluting the saponification liquid with water previous to the back titration.

The saponification value of the evaporation residue of pure bergamot oils lies between 136 and 200. The addition of 1 p.c. triethyl citrate increases the saponification value of the evaporation residue by 47.7. If one considers that 1 g. of triethyl citrate requires as much alkali for saponification as 2.13 g. linalyl acetate, it becomes apparent that *e. g.* 2 p.c. of added citric acid ester . will increase the apparent linalyl acetate content of the oil by 4.3 p.c., *i. e.* by an amount which under certain circumstances may suffice seemingly to bring an oil poor in ester up to the normal standard.

Noteworthy is the behavior of oils thus adulterated during saponification. Whereas pure bergamot oils yield clear solutions with alcoholic potassium hydroxide, those adulterated with citric acid ester are rendered turbid more particularly at the beginning of the saponification because of the formation of potassium citrate which is difficultly soluble in alcohol.

In order to prove the presence of citric acid, as such, the *calcium test* may be applied. 2 g. of oil or the evaporation residue of 5 g. of oil are saponified with alcoholic potassium hydroxide, the solution diluted with water, neutralized with hydrogen chloride, the alcohol evaporated from a water bath, the solution shaken out with ether and then filtered. The filtered solution is rendered slightly alkaline with sodium hydroxide, a few drops of concentrated calcium chloride solution are added and the mixture heated. The presence of citric acid is indicated by the formation of a precipitate, which, however, may require some time to form.

More decided is the reaction according to G. Denigès[1]), whereby the citric acid is converted into acetone dicarboxylic acid, which, in turn, yields a difficultly soluble mercury double salt. For this purpose 10 ccm. of the above solution are thoroughly shaken with 1 to 1.5 g. of lead superoxide, 2 ccm. of mercuric sulphate solution[2]) are added and the mixture filtered. 5 ccm. of the filtrate are heated to boiling and to this as much 2 p.c. potassium permanganate solution is added drop by drop until the solution is no longer decolorized immediately. In the presence of citric acid the addition of the first drop results in the formation of a flocculent, white or light yellow precipitate.

This reaction is much more delicate than the calcium test. With some practice it is even possible to approximate the citric acid ester content of the oil to be examined by comparing the results with those obtained from oils of known citric ester content. Great care should, however, be exercised with the addition of the potassium permanganate, for otherwise manganese peroxide may be precipitated, which may be mistaken for the precipitate described above (double salt of mercury and acetone dicarboxylic acid).

When six samples of bergamot oil, guaranteed pure, where tested by Schimmel & Co.[3]), according to Denigès' method, two of these revealed traces of citric acid. This small amount may have been introduced from the pulp rich in citric acid during the process of expression. As a matter of fact the traces were so slight that they need not be taken into consideration in practice. If, however, but 1 p.c. of triethyl citrate be added to such an oil, Denigès' test yields a precipitate ten times as voluminous. Moreover, the evaporation residue of these authentic oils revealed low saponification values; if the latter exceed 200, the oil may be regarded as suspicious.

METHOD OF PROCEDURE FOR THE DETERMINATION OF ALL OF THE ESTERS. In order that none of the above-mentioned esters may be overlooked in the course of the examination, it is

[1]) Bull. Soc. ph. de Bordeaux 1898, 33. — Compt. rend. 128 (1899), 680; Pharm. Zentralh. 89 (1898), 396.

[2]) To be prepared from 5 g. mercuric oxide, 20 ccm. conc. sulphuric acid and 100 ccm. water.

[3]) Report of Schimmel & Co. October 1910, 63.

expedient to proceed in the following manner: For the saponi-
fication four experiments are carried out as directed on p. 69.
If the difference of the saponification values obtained by fractional
saponification does not exceed 4, an adulteration with terpinyl
acetate has not been practiced. If the difference be greater,
the extent of the addition of terpinyl acetate can be approximated
by reference to the table on p. 70. In addition the saponification
value II is to be determined for one of the one-hour saponifi-
cation experiments by means of distillation with water vapor.
This S. V. II is to be compared with the regular saponification
value (A.V. + E.V.!). If the difference is greater than 10,
adulteration with esters of non-volatile acids may be assumed.
Provided sufficient material is available, it ought not to be
difficult to identify the acid in question. The test for glyceryl
acetate is carried out as described on p. 70.

The procedure here described is of general applicability for
the examination of oils with the mentioned adulterants. Thus
it may be applied to lavender oil and petitgrain oil which are
likewise judged in accordance with their ester content.

422. Bergamot Leaf Oil.

According to S. Gulli[1]) the distillation of *bergamot leaves*
is conducted on a restricted scale. It is practiced between
February and April when the trees are cleaned and trimmed.
The yield is small (100 kg. of leaves yield but 150 g. oil) and
the entire output for a year is said not to exceed 20 to 25 kg.
The pure oil has a specific gravity of about 0.870 to 0.873, an
optical rotation of + 25 to + 26°. It is soluble in an equal
volume of 90 p.c. alcohol. It contains about 32 to 34 p.c. of
esters, computed as *linalyl acetate,* some of which, however, is
methyl anthranilate.

The oil is rarely met with in a pure condition. Frequently
the bergamot leaves are distilled with the addition of turpentine
oil. Still more frequently the young plants of the bitter orange
tree are admixed. Rind oils also are used freely as adulterants.
However, the oil is not only adulterated itself, but it in turn is
used for the adulteration of petitgrain oil and orange flower oil,
both bitter and sweet. ·

[1]) Chemist and Druggist 60 (1902), 995.

423. Citron Oil.

Cedro- or Cedratöl. — Essence de Cédrat. - Essenza di Cedro. Essenza di Cedrino.

· **Origin.** According to S. Gulli[1]) the following citron varieties are cultivated in Calabria and Sicily:

1. *Citrus medica,* var. *vulgaris,* Risso, known in Calabria and in Sicily as *Cedro*; 2. *Citrus medica,* var. *gibocarpa* or *citrea,* Risso, designated *Cedrino*; and 3. *Citrus medica,* var. *rhegina,* Pasquale, known by the name *Cedrone.*

However, in commerce these three varieties are not commonly differentiated. • As a rule these fruits are not used for the production of volatile oil but, pickled in brine, they are exported, the one that is most sought being the one designated *cedrone.*• Citron oil is produced by expression from the first two varieties, and then usually on request only at the time of harvesting the fruit in Sicily and in Reggio-Calabria. It is rarely found in a pure condition since the manufacturers add to it minor or larger amounts of lemon or orange oils or the oil of the "süsse (sweet) Limone"[2]).

The oil of the third variety, known as *cedrone,* does not appear to be known.

Properties. Although the oils from the fruits known as *cedri* and *cedrini* are not kept separate in commerce, nevertheless they possess distinctive properties.

1. OIL OF CEDRO OR CEDRAT. d_{15} 0.8706[3]) and 0.871[4]); α_D 67°[3]) and + 67°8′[4]).

2. OIL OF CEDRINO. d_{15} 0.850 to 0.854; α_D : 77 to 81°; n_{D20}, (one determination) 1.47519[5]).

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[1]) Chemist and Druggist 60 (1902), 19.

[2]) For an oil prepared from the "süsse Limone" Schimmel & Co. (Report of Schimmel & Co. April 1903, 39) ascertained the following constants: d_{15} 0.8579; α_{D21} , 64 15′; n_{D20} 1.47568. It smells of citral. According to E. Bonavia, The cultivated oranges and lemons of India and Ceylon, London 1888, p. 67, the parent plant of the "sweet lemon" is *Citrus Lumia,* Risso.

[3]) S. Gulli, Chemist and Druggist 60 (1902), 19.

[4]) Report of Schimmel & Co. October 1895, 13.

[5]) S. Gulli, Chemist and Druggist 62 (1903), 22. — Report of Schimmel & Co. April 1903, 33 to 35.

Composition. An oil of cedro or cedrat has been examined by Schimmel & Co.[1]). Upon distillation the bulk of the oil passed over between 177 and 220°. The presence of *citral* was demonstrated by boiling with an alcoholic solution of β-naphthylamine and pyruvic acid, yellow crystalline laminæ of citryl-β-naphthocinchoninic acid melting at 197 to 200° resulting.

H. E. Burgess[2]) has examined an oil which he regards as cedro oil, but which Gulli[3]) proved to be a cedrino oil. The bulk of the oil consisted of terpenes: according to Burgess mostly *limonene* with some *dipentene* (derivatives not mentioned). That portion of the oil which passes over between 64 and 85 under a pressure of 10 mm. contains citral. With cyanacetic acid it yielded citralidene cyanacetic acid. Determined according to the bisulphite method the citral content averaged 6 p.c., according to the hydroxylamine method 5.7 p.c.

In the bottle of the examined oil a deposit had been formed. By solution in chloroform a crystalline compound $C_{18}H_{18}O_{6}$ was isolated that melted at 145° and probably is identical with citroptene (comp., however, formula on p. 29).

424. Oil of Limes.

Oleum Limettae. — Oil of Limette (Hand pressed Oil of Limette, Lime oil. Ecuelled Essence of Limes and Distilled Oil of Limes or Limette, Distilled Lime Oil). — Westindisches Limettöl. — Essence de Limette.

Origin and Production. The oil known in commerce as oil of limes is produced in the West Indies from the fruits of *Citrus medica*, L., var. *acida*, Brandis. The lime tree is cultivated in the West Indies, more particularly in the islands of Montserrat[1]), Dominica[1])[5])[6]), Jamaica, Trinidad[7]), Antigua[8]), Martinique,

[1]) Report of Schimmel & Co. October 1895, 13.

[2]) Analyst 26 (1901), 260; Chem. Zentralbl. 1901, II. 1226.

[3]) S. Gulli, Chemist and Druggist 62 (1903), 22. — Report of Schimmel & Co. April 1903, 33 to 35.

[4]) Pharmaceutical Journ. 82 (1909), 19.

[5]) H. A. Tempany & N. Greenhalgh, West Indian Bull. 12 (1912), 498; Report of Schimmel & Co. April 1913, 72.

[6]) Report of Schimmel & Co. October 1904, 54.

[7]) E. M. Holmes, Essence of Limes from Trinidad. Pharmaceutical Journ. III. 14 (1884), 1005.

[8]) H. A. Tempany & T. Jackson, West Indian Bull. 12 (1912), 504.

St. Lucia[1]) and Barbadoes. The common *C. medica,* var. *acida,* Brandis has very spiny branches. Some years ago H. Green introduced a less spiny variety which produces a smaller but more juicy fruit[2]). Whether the oils of the two varieties differ has not yet been ascertained.

The limes are exported in part as such. Oil is produced from these principally in Montserrat and Dominica. In Montserrat the *Ecuelle à piquer* is said to be used, an instrument formerly employed in Nice in the production of agrumen oils. It consists of a hemisphere provided with erect brass needles and at the bottom with a tube. The fruits scratched by the needles emit their oil which collects in the tube and thence is transferred from time to time to a container. In Dominica a machine is said to have proven successful[3]). It was invented by W. A. D. Allport and T. I. W. C. Davenport[4]) and its construction is indicated in the Journ. Soc. Chem. Ind. 30 (1911), 1138. The distilled oil described below is inferior and is obtained by distillation of the fruit rinds, also as a byproduct in the evaporation of lime juice used for the production of citric acid.

Statistical data are available only for Dominica[5]) where about 2000 hectares (abt. 5000 acres) are planted with limette trees. During the last 30 years the limette industry has rapidly developed in this island. The first plantings date from the year 1850. In 1910, there were exported 5761 gals. of distilled and 1018 gals. of expressed oil representing the respective values of s 16823.00 and s 11767.00. For the year 1911 the exports amounted to 5472 gals. of distilled and 892 gals. of expressed oil representing the values of s 15989.00 and s 10317.00 respectively.

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[1]) Chemist and Druggist 83 (1913), 261. Comp. also Report of Schimmel & Co. April 1914, 68. (*Eucalyptus paniculata* is cultivated as a protection to the lime plantations.)

[2]) Journ. d'Agriculture tropicale 8 (1908), 283. — G. A. Jones, West Indian Bull. 12 (1912), 507.

[3]) Daily Consular and Trade Reports, Washington; Report of Schimmel & Co. April 1918, 72.

[4]) U. S. Pat. 1002020.

[5]) Daily Consular and Trade Reports, Washington. Report of Schimmel & Co. April 1913, 73.

EXPRESSED WEST INDIAN OIL OF LIME.

Properties. It is of a golden yellow color. Aside from the
greater intensity of the odor, it can scarcely be distinguished
from a good lemon oil. d_{15} 0.878 to 0.901, usually between 0.880
and 0.884; α_{D} · 32 to   38 ; so far as the few observations admit
of any conclusions, the first 10 p.c. of the distillate (comp.
under Lemon Oil, p. 43) deviate slightly higher or at most but
4 lower than the original oil. $n_{D20°}$ 1.482 to 1.486; evaporation
residue 10 to 18 p.c. S.V. of the residue 160 to 181. With 4 to
10 vol. of 90 p.c. alcohol the oil forms a turbid solution showing
a slight bluish fluorescence and separating waxy constituents.
The citral content determined by the phenylhydrazine method
was 6.5 to 9 p.c. According to the method of Burgess (see Vol. I,
p. 584), Tempany and Greenhalgh[1]) found but 2.2 to 6.6 p.c.

The principal constituent of the expressed limette oil is
citral. The terpenes do not appear to have been investigated.
In the high boiling fractions methyl anthranilate[2]) may be
contained. In addition the presence of *bisabolene* has been
demonstrated[3]). As is the case with other expressed oils,
a sediment is formed on standing. From it a crystalline
substance $C_{11}H_{10}O_4$ melting at 147.5′ has been isolated. It
was named limettin by W. A. Tilden[4]) but E. Schmidt[5]) has proven
it to be identical with *citroptene* (see p. 29 for formula).

DISTILLED WEST INDIAN LIMETTE OIL.

Properties. Very different from the expressed oil is the oil
which is obtained as a byproduct during the evaporation of the
juice and which enters commerce as "oil of limes". Its odor is
unpleasant, turpentiny and no longer reminds of citral. Presumably
this aldehyde is completely destroyed when the acid liquid is
boiled. $d_{15°}$ 0.860 to 0.870; α_{D} ÷ 33 to   47°; $n_{D20°}$ 1.4702 to 1.4707.
In connection with 3 samples Tempany and Greenhalgh[6]) found

[1]) p. 78, footnote 5.

[2]) Tempany and Greenhalgh, *loc. cit.*

[3]) H. E. Burgess and T. H. Page, Journ. chem. Soc. 85 (1904), 414.

[4]) *Ibidem* 61 (1892), 344. — W. A. Tilden & H. Burrows, Proceed. chem.
Soc. 17 (1901), 216.

[5]) Arch. der Pharm. 242 (1904), 288.

[6]) *Loc. cit.* and *ibidem* 1329.

1.2 to 2.0 p.c. of citral when assayed according to the sulphite method. However, this citral content may be but apparent since citral as such was not proven present in the oil.

Composition. According to Burgess and Page[1] distilled limette oil contains in the middle range of fractions l-*α-terpineol* (m. p. 35`; m. p. of nitrosochloride 105 to 106`; m. p. of nitrolanilid 150 to 151 ; m. p. of phenylurethane 111`; m. p. of ketolactone 62 ; m. p. of oxime of ketolactone 77`) and a second alcohol which boils at a slightly lower temperature, the phenyl urethane of which crystallizes in needles and melts at 132`. In the high boiling fraction *bisabolene* (limene) was found (m. p. of trihydrochloride 79 to 80`[1])).

. **425. Oil of Limette Leaves.**

An oil obtained from the Imperial Institute in London was examined by Schimmel & Co.[2] It had been distilled in Dominica from *limette leaves* from *Citrus medica*, L., var. *acida*, Brandis. It was light yellow in color and its odor resembled slightly that of the oil expressed from the fruit rinds, but was more lemongrass-like. d_{15} 0.8783; $α_D + 37°30'$; A.V. 3.6; E.V. 23.0; soluble in 0.5 vol. of 90 p.c. alcohol, but upon the addition of more than 4 vol. of solvent the solution became opalescent. Presumably the 43 p.c. of the oil which reacted with bisulphite consisted exclusively of citral. A more careful analysis was impossible because of the small amount of oil available.

A sample of limette leaf oil received by the Imperial Institute[3] in London from Montserrat showed the following properties: d_{15} 0.8772; $α_D : 38°17'$; S.V. 27.6; soluble in 90 p.c. alcohol, the diluted solution (1:9) showing opalescence. 43 p.c. of the oil reacted with bisulphite solution.

According to F. Watts[4] the oil of the leaves of *Citrus Limetta* contains an inactive terpene which boils at 176 to 177° and which yields a crystalline hydrochloride melting at 49 to 50°, hence is *dipentene*. A ketone boiling between 220 and 230°

[1]) *Loc. cit.* and *ibidem* 1329.
[2]) Report of Schimmel & Co. October 1910, 79.
[3]) Bull. Imp. Inst. 11 (1913), 436.
[4]) Journ. chem. Soc. 49 (1886), 316; Chem. Zentralbl. 1886, 407, 837.

yielded pelargonic acid when oxidized with chromic acid in acetic acid solution, and for this reason was regarded as *methyl nonyl ketone*.

426. Italian Limette Oil[1]).

Origin and Production. The fruits of the South European limette, *Citrus Limetta*, Risso[2]) (*Citrus Limetta vulgaris, Lima dulcis, Lima di Spagna dolce, Limettier ordinaire*) differs from the West Indian by their sweet juice.

In Calabria the limette tree is known as *Arancio* or *Limon-cello di Spagna*, its fruits as *Aranci* or *Limi di Spagna*. Formerly the limette trees were cultivated in large numbers for the bergamot was grafted upon them. Inasmuch, however, as their roots are frequently attacked by the socalled gum disease, the bergamot is now grafted upon the more resistent bitter orange tree. The fruit of the Italian limette tree resembles the lemon but is more spherical, also the strongly developed nipple is broader and depressed. The oil can be obtained by expression but is no article of commerce. However, it has been prepared occasionally.

Properties. The oil obtained by expression of the fruit rind is brownish-yellow in color, has a strong odor reminding of bergamot, and upon standing deposits a solid in considerable amount. d_{15° 0.872; $\alpha_D + 58°19'$; S. V. 75.

Composition. Italian limette oil is similar in composition to bergamot oil, but contains more limonene and less linalyl acetate. The *limonene* in question is the dextrogyrate modification ($\alpha_D + 81°45'$; d_{15° 0.848) and yields a dihydrochloride[3]) melting at 50°, also a tetrabromide melting at 105°. The oil examined by Gildemeister contained 26.3 p.c. of *linalyl acetate* (b. p. 101 to 103° under 13 mm. pressure; d_{15° 0.898; $\alpha_D - 9°52'$). After

[1]) E. Gildemeister, *Über Limettöl.* Arch. der Pharm. 233 (1895), 175.

[2]) Risso et Poiteau, *Histoire et culture des Orangers.* II. Edition par M. A. Du Breuil. Paris 1872.

[3]) The same hydrochloride had already been obtained by S. de Luca (Compt. rend. 51 [1860], 258) from a terpene boiling at 180° which was reported as having been obtained from *Citrus Lumia* but which in all probability had been obtained from Italian limette oil. Comp. Gildemeister, *loc. cit.*

saponification with alkali, acetic acid was found in the mother
liquid. From the saponified oil *l*-linalool (b. p. 88.3 to 89.5°
under 13 mm. pressure; d_{15} 0.870; $[\alpha]_{D}$ - - 20 7') was fractionated
and upon oxidation[1]) yielded citral. The *linalool* is present
partly as free alcohol, partly as ester.

427. Limette Flower Oil.

E. J. Parry[2]) reports on the investigation of a limette flower
oil obtained from Messina. Presumably the oil was one obtained
from the flowers of *Citrus Limetta*, Risso. Its color was greenish-
yellow and it revealed the following constants: d 0.870; α_{D} · 21°30'.
When shaken with dilute hydrochloric acid a body was extracted
from the oil which yielded, on supersaturation of the acid liquid
with alkali, a fluorescent solution when shaken with ether. After
evaporation of the solvent an oil remained which had a decided
odor of orange flowers. It was saponified and the alkaline
solution acidified, whereupon an acid melting at 135 separated.
Hence Parry concludes the presence of anthranilic acid methyl
ester. (Pure anthranilic acid melts at 144 to 145°.)

From the oil shaken with hydrochloric acid a fraction boiling
between 195 and 200 was obtained. It had the specific gravity
0.874 and appeared to be *linalool*.

428. Oil of Mandarins.
Oleum Mandarinae. Oil of Tangerines. Mandarinenöl. Essence de Mandarines.

Origin. The rind of the mandarin, the well-known fruit of
Citrus madurensis, Lour. (*C. nobilis*, Lour.)[3]) contains a very
agreeable volatile oil which, like the other oils of the agrumen fruits,
is obtained by expression. 1000 fruits yield about 400 g. of oil.[4])

Properties. Oil of mandarin is a golden-yellow liquid with
a slight bluish fluorescence which becomes more prominent

[1]) To which ·substance the limettic acid $C_{11}H_4O_6$ obtained by H. Vohl
(Arch. der Pharm. 124 [1853], 16; Pharm. Zentralbl. 1853, 318) owes its origin
is uncertain.

[2]) Chemist and Druggist 56 (1900), 993.

[3]) According to some authorities *C. madurensis*, Lour. is synonymous
with *C. nobilis*, Lour., according to others it is not.

[4]) E. Bertè & S. Gulli, *Sull' analisi della essenza di mandarino*. Messina
1905; Report of Schimmel & Co. October 1905, 31.

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when the oil is diluted with alcohol. The odor is agreeably refreshing, d_{15} 0.854 to 0.859; α_D : 65 to 75°; α_D of the first 10 p.c. of distillate (comp. under Oil of Lemon, p. 43) slightly lower or but 2 p.c. higher than that of the original oil. According to E. Bertè and G. Romeo[1] the α_D of the first 50 p.c. should average 3° higher than the original oil; n_{D20} 1.475 to 1.478; A. V. up to 1.7; E. V. 5 to 11; E. V. after acetylation 12.5 (1 determination); evaporation residue 2.4 to 3.5 p.c.; soluble in 7 to 10 vol. of 90 p.c. alcohol with more or less turbidity.

A Spanish oil from the province of Valencia, which had been expressed from the *immature fruits*, had an olive-green color and an agreeable odor, but less delicate than that of the oil from ripe fruits. Its physical constants also revealed deviations: d_{15} 0.8665; n_{D20} 1.47900; A.V. 0.2; E.V. 17.3; evaporation residue 8 p.c. On account of the dark color, the angle of rotation of the original oil could not be observed. The first 10 p.c. of the distillate showed α_D + 55°12'. In 90 p.c. alcohol the oil was not completely soluble, but it formed a clear solution with 0.5 vol. and more of 95 p.c. alcohol[2]).

Two mandarin oils[3]) *distilled* in Porto Alegre, Brazil, revealed the following properties: d_{15} 0.8515 and 0.8510; α_D + 74°16' at 17° and +74°20' at 16°. Both oils were characterized by a beautiful blue fluorescence.

Composition. The larger part of mandarin oil consists of d-*limonene*. When brominated in glacial acetic acid solution, fraction 175 to 177° (α_D 76°45') yielded a tetrabromide[4]) melting at 104 to 105°. With hydrogen chloride the same fraction yielded dipentene dihydrochloride melting at 49°[5]).

If the residual oil, left above 177°, is treated with bisulphite solution, an addition product results from which alkali separates an oil which upon condensation with pyruvic acid and β-naphthylamine, yields a naphthocinchoninic acid the melting point of which is not constant. At 197° this substance softens but does

[1]) *Annali del laboratorio chimico della camera di commercio ed arti della provincia di Messina*. Messina 1908; Report of Schimmel & Co. April 1909, 51.

[2]) Report of Schimmel & Co. October 1911, 46.

[3]) *Ibidem* April 1896, 62.

[4]) E. Gildemeister & K. Stephan, Arch. der Pharm. 235 (1897), 583.

[5]) S. de Luca, Compt. rend. 45 (1857), 904.

not melt until 222°. Which aldehydes correspond to this compound is not known.

The principal constituent of the oil to which is due the characteristic odor as well as the fluorescence, is the *methyl anthranilic acid methyl ester*, a substance found by H. Walbaum[1]) in 1900.

From 5 kg. of mandarin oil 36 g. of a base were obtained by shaking with the sulphuric acid, the bulk of which distilled between 130 and 131° (13 mm.). Its specific gravity was 1.120 at 15°. In the cold it congealed and melted at 18.5 to 19.5 . This compound forms salts and double salts and its odor is similar to that of anthranilic acid methyl ester. When heated with hydroiodic acid it decomposes with the formation of methyl iodide. Alcoholic potassium hydroxide saponifies the ester and from the salt solution acetic acid precipitates the methyl anthranilic acid.

This acid melts at 179 . When heated with dilute hydrochloric acid to from 160 to 170° it decomposes into carbonic acid and methyl aniline. It yields the same derivatives obtained by G. Fortmann[2]) from the synthetic methyl anthranilic acid, e. g. nitrosomethylanthranilic acid (m. p. 128°), acetylmethylanthranilic acid (m. p. 186°) and benzoylmethylanthranilic acid (m. p. 161°).

Synthetically the methyl ester of methylanthranilic acid

$$C_6H_4 \begin{array}{l} NH \cdot CH_3 ^{[1]} \\ COOCH_3 ^{[2]} \end{array}$$
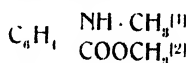
can be obtained by boiling the methyl alcoholic solution of methylanthranilic acid with sulphuric acid and subsequent decomposition of the ester salt with soda solution[3]).

Although mandarin oil contains scarcely 1 p.c. of this substance, it is of greatest importance so far as the odor of the oil is concerned.

Quantitatively[4]) the amount of ester can be determined as its anthranilic acid methyl ester. (Comp. vol. I, p. 544.)

[1]) Journ. f. prakt. Chem. II. 62 (1900), 135.
[2]) *Ibidem* II. 55 (1897), 123.
[3]) The constants of the synthetic ester may be found in vol. I, p. 543.
[4]) A. Hesse & O. Zeitschel, Berl. Berichte 34 (1901), 296; 35 (1902), 2355.

429. Oil of Mandarin Leaves.

Mandarin Petitgrain Oil. — Mandarinenblätteröl. — Essence de Petitgrain mandarinier.

Production. Upon distillation with water vapor, the leaves of the mandarin tree yield from 0.2 to 0.35 p. c. of volatile oil which in the receiver usually separates into a lighter and a heavier oil.

Properties. A Spanish oil described by Schimmel & Co.[1]), which had been obtained from Carcagente, was yellowish in color and showed a decided bluish fluorescence, $d_{15°}$ 1.0142; $\alpha_D + 7°46'$; E. V. 216; soluble in 6 to 6.5 vol. of 80 p. c. alcohol. The properties of an oil from southern France[2]) were: $d_{15°}$ 1.005; $\alpha_D + 7°19'$; S. V. 159. Another oil from the same source[3]) had d_{15} 1.0643; $\alpha_D + 2°20'$; S. V. 265.

The oil examined by E. Charabot[4]) (see under Composition) deviated the polarized light $+ 6°40'$; S. V. 160, content of methyl anthranilic acid methyl ester about 50 p. c.

Upon the distillation of 250 kg. of leaves in Grasse, A. Hesse[5]) obtained 618 g. of light oil and 159 g. of heavy oil. The former showed d_{15} 0.993; $\alpha_D + 5°42'$; S. V. 191; content of methyl anthranilic acid methyl ester 55.7 p. c. (accurately determined according to the method worked out for anthranilic acid methyl ester, see vol. I, p. 544). The heavy oil showed d_{15} 1.033; $\alpha_D + 3°20'$; S. V. 238; content of methyl anthranilic acid methyl ester 67.65 p. c. Both oils congealed in a freezing mixture. From the aqueous distillate an additional 80 g. of oil were obtained that contained over 80 p. c. of ester. The methyl anthranilic acid methyl ester content of the total oil was computed at 65 p. c. There were also found in this leaf oil a small amount of other esters, likewise a non-saponifiable base with an odor of nicotine.

[1]) Report of Schimmel & Co. October 1902, 83.

[2]) *Ibidem* April 1902, 81.

[3]) Berichte von Roure-Bertrand Fils, October 1910, 42.

[4]) Compt. rend. 135 (1902), 580.

[5]) Chem. Zeitschr. 2 (1903), 497.

Composition. As shown by E. Charabot[1]) mandarin leaf oil consists principally of *methyl anthranilic acid methyl ester*[2]). It was isolated and identified according to the method employed by H. Walbaum in his investigation of mandarin oils. The melting point of the ester was 19˚. It was identified as methyl anthranilic acid methyl ester by elementary analysis and by the acid obtained upon saponification which melted at 179˚ and showed all of the properties of methyl anthranilic acid.

430. Grape Fruit Oil.

The rind of the grape fruit or shaddock, Ger. *Pompelmus*, from *Citrus decumana*, L. which attains a weight of 6 kg. contains a small amount of volatile oil that can be obtained by expression or distillation.

An expressed oil[3]), obtained from fruits from Orlando, Florida, possessed a very pleasant odor reminding of bitter orange oil. d_{15} 0.860; α_{D} +94 30'.

In the Philippines several varieties of grape fruit seem to exist: one with large leaves that possesses almost no oil cells, and one with small leaves, from which B. T. Brooks[4]) obtained 1.7 p.c. of an oil with a pleasant odor: d_{30}^{30} 0.8700; α_{D30} 22.90 (: ?); n_{D30} 1.4644; E.V. 10; soluble in 70 p.c. alcohol. It contains 25 p.c. of *dipentene* (m. p. of tetrabromide 120˚), 15 p.c. *linalool* (characterized by its boiling point and its oxidation to citral), and 1 p.c. of an aldehyde that reacts with bisulphite and has a citral-like odor.

[1]).Compt. rend. 135 (1902), 580.

[2]) E. Charabot und G. Laloue (Compt. rend. 137 [1903], 996. – Bull. Soc. chim. III. 31 [1904], 195) have made a study of the origin of the volatile oil, more particularly of the methyl anthranilic acid methyl ester, in the leaves and petioles of the mandarin tree. It was found that the formation of the volatile oils in the leaves is most active while there organs are young. Moreover, the leaves contain more oil than the petioles. Later the terpene content of the leaves is diminished whereas that of the petioles is increased. The water-soluble constituents (methylanthranilic acid methyl ester) seem to accumulate in the leaves during the process of vegetation, the reverse being true of the petioles.

[3]) Report of Schimmel & Co. April 1894, 57.

[4]) Philippine Journ. of Sc. 6 (1911), A, 349.

431. Oil of Neroli.

Oleum florum Aurantii. — Orangenblüten- or Neroliöl. — Essence de Néroli.

Origin and Production. Oil of neroli is distilled from the
esh flowers of the bitter orange, *Citrus Bigaradia,* Risso
. *Aurantium,* L. subspec. *amara,* L.), more particularly in
e Département des Alpes-Maritimes of southern France. The
llowing localities are noteworthy because of their larger
·oves: Cannes, Le Cannet, Vallauris and Golfe Jouan, also the
llowing localities near to the base of the Maritime Alps, *viz.*
iot, Cagnes, La Colle, La Gaude, Gattières, St. Jeannet, Vence,
ourettes, Gorges du Loup, and Le Bar. ·

The principal harvest of blossoms lasts from the beginning
f May to the middle·of June and, in good years, amounts to
om 2.5 to 3 million kg. Much smaller is the harvest of fall
lossoms[1]). In 1909 it amounted to 270000 kg. The flowers
re collected by women with the aid of ladders. Each blossom
as to be pinched off with the finger nails and is dropped on
lothes spread underneath the tree. Only the fully expanded
owers are picked and all injury to the buds must be carefully
voided. In order to obtain satisfactory prices for the flowers,
1e owners of the groves have not long ago combined them-
elves to a syndicate *(Société coopérative de production des
ropriétaires d'orangers des Alpes-Maritimes),* which uses the
owers not sold to others. The price of the blossoms fluctuates
etween 0.5 to 1.35 fr. per kilogram. Most of the flowers are
listilled and only such oil is collected as separates directly in
he receiver. The aqueous distillate is not cohobated, but sold
is orange flower water *(Aqua florum Aurantii, aqua Naphæ),*
 kg of water being distilled from 1 kg. of flowers. The yield of
iil thus obtained varies between 0.086 and 0.0148 p.c. About
ine-third of the oil remains in the water. Upon distillation
if fresh orange flowers, which, for export purposes, are pre-
served either with salt or brine, Schimmel & Co.[2]), obtained
ipproximately 0.1 p.c. of oil.

[1]) For details as to yield see Report of Schimmel & Co. October 1899, 38;
)ctober 1902, 52; October 1903, 49. — P. Jeancard & C. Satie, Bull. Soc. chim.
II. 23 (1900), 605 and 29 (1903), 992.

[2]) Report of Schimmel & Co. October 1891, 34 and October 1894, 39.

The stills used in southern France have a capacity of from 600 to 800 liters. Each is charged with 300 to 350 kg. of flowers and 400 to 450 liters of water ($1^1$₂ times the amount of flowers). The distillation lasts $2^1$₂ to 3 hours and at first is carried on with ½ atmosphere pressure, later with 1 atmosphere and finally with $1^3$₄ to 2 atmospheres [1]).

Other methods for extracting the perfume of the orange blossoms are maceration [2]) and extraction [3]) with volatile solvents. The former is conducted on a small scale only. The latter is coming into greater favor in recent years since the product thus obtained best resembles the perfume of the plant. A. Hesse and O. Zeitschel [4]) have extracted the orange blossoms with petroleum ether. The extract thus obtained was triturated with alcohol and the alcoholic solution freed from plant wax by freezing. The oil obtained upon evaporation of the alcohol in vacuum was distilled with water vapor and the aqueous distillate extracted with ether. The oil obtained after the evaporation of the ether was added to that which had separated from the aqueous distillate. In this manner 1000 kg of orange blossoms yielded 806 g. of extracted orange flower oil. (For the constants of this oil see Properties.)

According to Roure-Bertrand Fils [5]) the amount of extractive obtained by treating the blossoms with petroleum ether is greater for the spring flowers than for the fall flowers. In the former instance the yield was 0.2272 p.c., in the latter 0.1795 p.c.

As to the formation of volatile oil in the several parts of the orange tree, detailed investigations have been made by E. Charabot and G. Laloue [6]).

In order to ascertain which of the several methods is the most rational for the extraction of the perfume, Hesse and Zeitschel [7]) have made a comparative study. They arrived at

[1]) L. Mazuyer, Journ. Parfum. et Savonn. 21 (1908), 134.

[2]) Comp. vol. I, p. 264.

[3]) Comp. vol. I, p. 247.

[4]) Journ. f. prakt. Chem. II. 66 (1902), 512.

[5]) Berichte von Roure-Bertrand Fils April 1910, 48. — G. Laloue, Bull. Soc. chim. IV. 7 (1910), 1101.

[6]) Compt.rend.138(1904),1229,1513. — Bull.Soc.chim.III.31(1904),884,937.

[7]) Journ. f. prakt. Chem. II. 64 (1901), 245.

the conclusion that distillation produces the largest yield. Then follows extraction with about one-half of the former yield and finally maceration with only one-third as much oil. Quite irrational is the enfleurage method which yields but one-fifteenth.

The influence of the weather on the yield, also on the properties of the oil, has been studied by Jeancard and Satie[1]), likewise by J. Gras[2]).

Although the bitter orange tree is widely distributed in the countries along the Mediterranean, its flowers are distilled but rarely outside of southern France. Occasionally small amounts of Spanish oil enter the market, also Syrian, Italian, and Algerian oils. These as well as oils of other origin are enumerated under Properties.

Properties. The neroli oil of commerce, *i. e.* the oil obtained as a byproduct in the distillation of orange flower water, is a yellowish oil which becomes brownish-red when exposed to light, and is slightly fluorescent. It has an intense, very pleasant odor of the orange blossoms and a somewhat bitter, aromatic taste. d_{15} 0.870 to 0.881; $a_D + 1°30'$ to $+9°8'$, as a rule not above $+7°$[3]); n_{D20} 1.468 to 1.474; A. V. up to 1.8; E. V. 19 to 69; content of anthranilic acid methyl ester 0.45 to 1.1 p.c. (For the method of assay[4]) see vol. I, p. 543.)

The oil is soluble in 1 to 2 vol. of 80 p.c. alcohol. The addition of more solvent causes the solution to become turbid, which upon standing separates small crystals of paraffin at the

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[1]) Bull. Soc. chim. III. 23 (1900), 605; 25 (1901), 934; 29 (1903), 992.

[2]) Report of Schimmel & Co. October 1901, 38; October 1905, 49.

[3]) Roure-Bertrand Fils (Berichte April 1910, 48) point out that lævorotation is characteristic of the neroli oils obtained by extraction, whereas the oils obtained by distillation of the blossoms with water vapor are dextrogyrate. Hence the latter method causes an inversion of the rotation, at least when the distillation is conducted under atmospheric pressure. When distilling under diminished pressure the same firm obtained a laevogyrate oil ($a_D - 2°30'$) which, moreover, closely resembled the extract oil as to odor. In connection with an oil distilled according to the ordinary manner from flowers in the fall of 1909, a dextrorotation of $+9°8'$, the highest thus far recorded, was observed.

[4]) G. Laloue[*] (Bull. Soc. chim. IV. 7 [1910], 1101) suggests that, for the protection of the other constituents, 'the oil be diluted with 6 vol. in place of 2 or 3 vol. of ether, that the precipitation be carried out at $-4°$ and that the filtrate be cooled with ice water.

surface. The alcoholic solution of neroli oil is characterized by a handsome violet-blue fluorescence, which is brought out beautifully when alcohol is superimposed on oil. When strongly cooled the oil looses its transparency because of the separation of paraffin and, at times, congeals to a butyraceous mass.

In order to acquaint themselves with the properties of oils, the genuineness of which could not be questioned, Schimmel & Co.[1]) distilled several lots of fresh orange blossoms some of which were preserved with salt, others with sea water. A yield of approximately 0.1 p.c. of oil was obtained showing the following constants.

No.	d_{15}	α_D	S. V.	Behavior in freezing mixture
1	0.887	inactive	41	Congealed to a butyraceous mass.
2	0.881	—	36	
3	0.876	0 52'	21	Became viscid, but did not congeal
4	0 872	0 40'	21	

Because of its dark color, the angle of rotation of No. 2 could not be determined. Nos. 3 and 4 are oils from the same lot of flowers. No. 4 consists of only such oil as separated from the aqueous distillate in the receiver.

Properties of the Orange Flower Oil obtained from the Aqueous Distillate. The oil obtained by salting out and shaking out the oil from the aqueous distillate with ether had the following properties[2]): d_{15} 0.945 to 0.968; α_D + 1° 47' to + 2 30'; S. V. 49 to 100 content of methyl anthranilate 11.6 to 16 p.c.

Properties of the Extract Oil. Upon extraction of the orange flowers with petroleum ether and subsequent distillation of the extract, after removal of the solvent, with water vapor, an oily and an aqueous distillate are obtained. If the aqueous distillate is salted out and shaken with ether, and the oily residue obtained upon evaporation of the ether added to the original oil, a total oil is obtained possessing the following

[1]) Report of Schimmel & Co. October 1891, 34 and October 1894, 39.
[2]) Hesse and Zeitschel, Journ. f. prakt. Chem. II. 64 (1901), 250, 258, 66 (1902), 506.

properties[1]): $d_{15°}$ 0.889 to 0.929, α_D — 0° 48' to — 4° 6', S. V. 55 to 118, anthranilic acid methylester content 2.7 to 15 p.c.

Properties of the Enfleurage Oil. $d_{15°}$ 0.909; α_D + 8° 34'; S. V. 58.2, methyl anthranilate content 5.2 p.c.[1])

Properties of the Pomade Oil. d_{15} 0.913; α_D — 5°; S.V. 78.1, methyl anthranilate content 9.2 p.c.[2])

Properties of neroli oils not distilled in southern France. Although there appears to be no reason why other districts should not produce first-class oils, it would appear from the properties of the oils hereinafter enumerated that thus far no oils have been produced that can compete with those from southern France. Possibly this may be attributed to the lack of sufficiently careful selection of the material used for distillation. If in place of the fully expanded flower, buds or twigs, leaves and unripe fruits are utilized, oils are obtained which resemble the petitgrain oils more or less.

With few exceptions, the following oils have been examined in the laboratory of Schimmel & Co. The number in parentheses behind the geographic designation indicates the number of samples examined.

SPAIN (7).

$d_{15°}$ 0.870 to 0.885; α_D + 9° 30' to + 29°; $n_{D20°}$ 1.4705 to 1.4720; A. V. 0.7 to 2.0; E. V. 18 to 47, methyl anthranilate content 0.45 to 0.5 p.c.[3])

CALABRIA AND SICILY (11).

$d_{15°}$ 0.860 to 0.924; α_D + 2° 54' to + 56° 30'; $n_{D20°}$ 1.468 to 1.474; A. V. 0.3 to 1.0; E. V. 6 to 127, methyl anthranilate content (1 determination) 0.22 p.c.

VENEZUELA (2).

$d_{15°}$ 0.884 to 0.887; α_D — 0° 55' to — 1° 54'; $n_{D20°}$ 1.463 to 1.465; A. V. 1.3 to 1.9; E. V. 96 to 102.

PARAGUAY (1).

$d_{15°}$ 0.9076; α_D + 0° 25'; A. V. 6.0; E. V. 72.5.

[1]) Hesse and Zeitschel, *loc. cit.* 64 (1901), 250; 66 (1902), 513. — Report of Schimmel & Co. October 1903, 49. — Berichte von Roure-Bertrand Fils April 1910, 48. — G. Laloue, Bull Soc. chim. IV. 7 (1910), 1101.

[2]) Hesse and Zeitschel, *loc. cit.* 64 (1901), 250.

[3]) Report of Schimmel & Co. October 1903, 77.

MAYOTTE (I).

$d_{15°}$ 0.8562; α_{D} + 46 2'; n_{D20} 1.4705; E. V. 4.6.

ALGERIA.

d_{15} 0.8723 to 0.8768; α_{D} + 5 42' to + 6 6'; S. V. 72 to 91[1]).

SYRIA (I)

d_{15} 0.8758; α_{D} | 1 6'; S. V. 51.5[2]).

Composition. Neroli oil is of special interest to the perfume chemist because it is the first oil in which there has been found a nitrogenous substance of exceeding fragrance. Inasmuch as this valuable oil is indispensable to finer perfumery, it has recently been subjected repeatedly to scientific investigation. As a result the presence of a considerable number of substances has been established. The following compilation of constituents pertains to the ordinary neroli oil obtained by steam distillation.

l-α-*Pinene* (m. p. of pinene nitrolbenzylamine 122 to 123).[3]

l-*Camphene*. Upon treating fraction 168 to 170 ' with glacial acetic acid-sulphuric acid, H. Walbaum and O. Hüthig[3] obtained *iso*borneol which, however, melted at 195 instead of at 212. Neither did A. Hesse and O. Zeitschel[4] succeed in raising the melting point beyond 200° although they purified the *iso*borneol through its phthalic acid ester.

Dipentene was identified in fraction 175 to 179 ' (α_{D} – 1 6') by means of its tetrabromide (m. p. 125).[5] Previously F. Tiemann and F. W. Semmler[6] had obtained a tetrabromide melting at 105 from fraction 75[7] (15 mm.) and had concluded the presence of limonene. Apparently they did not examine the optical rotation of the fraction, hence it may be presumed that the tetrabromide melting per chance at 105° was an impure dipentene

[1]) A. Chapus, Journ. de Pharm. et Chim. VI. 30 (1909), 484. The material that was distilled consisted primarily of floral buds. -- Report of Schimmel & Co. October 1910, 88.

[2]) Berichte von Roure-Bertrand Fils April 1911, 26.

[3]) Report of Schimmel & Co. October 1902, 54 to 57. Journ. f. prakt. Chem. II. 67 (1903), 315 to 325.

[4]) Journ. f. prakt. Chem. II. 66 (1902), 481 to 516.

[5]) Report of Schimmel & Co. October 1902, 54 to 58. - Journ. f. prakt. Chem. II. 67 (1903), 315 to 325.

[6]) Berl. Berichte 26 (1893), 2711, footnote.

tetrabromide. If this explanation is rejected, it must be assumed
that the neroli oil in question was adulterated with orange oil,
for pure oils yield fractions with but a slight rotation from
which limonene tetrabromide cannot be obtained directly.

Decylic Aldehyde. From fraction 70 to 82˙ (7 to 8 mm.)
shaking with bisulphite separated a solid compound which, when
decomposed with alkali carbonate, developed the odor of decylic
aldehyde[1]). Inasmuch as characteristic derivatives of this alde-
hyde have not been prepared, its presence has not yet been
demonstrated. Its presence may, however, be regarded as
probable since it occurs in the closely related orange oil.

l-Linalool had first been found in the oil by Tiemann and
Semmler[2]). Its presence was definitely proven by Walbaum and
Hüthig[1]) who prepared its phenylurethane melting at 65˚.
According to Hesse and Zeitschel[3]) the oil contains about
30 p.c. of linalool, partly combined with acids.

l-Linalyl Acetate. According to Tiemann and Semmler[2])
fraction 97 to 104˚ (15 mm.; d_{20} 0.8972) consists of linalyl acetate.
When boiled with potassa, it was broken up into acetic acid and
linalool. The presence of this ester was proven a second time by Hesse
and Zeitschel[4]) who assumed that the oil examined by Tiemann and
Semmler was largely adulterated with petitgrain oil. This assumption
was not correct as demonstrated in detail by Walbaum and Hüthig.

Phenyl Ethyl Alcohol. This alcohol having been found by
Hesse and Zeitschel[4]) in the oil extracted from the orange flower
water, its presence in the oil proper was demonstrated by Walbaum
and Hüthig (oxidation to phenyl acetic acid).

α-Terpineol (m. p. above 33°; m. p. of terpinyl phenyl
urethane 112˚)[5])[6]).

Nerol. This alcohol, previously unknown, was discovered
by Hesse and Zeitschel[6]) in neroli oil. Its boiling point is

[1]) Report of Schimmel & Co. October 1902, 54 to 58. — Journ. f. prakt.
Chem. II. 67 (1903), 315 to 325.

[2]) Berl. Berichte 26 (1893), 853.

[3]) Journ. f. prakt. Chem. II. 64 (1901), 245 to 260.

[4]) Journ. f. prakt. Chem. II. 64 (1901), 245 to 260.

[5]) Report of Schimmel & Co. October 1902, 54 to 58. — Journ. f. prakt.
Chem. II. 67 (1903), 315 to 325.

[6]) Journ. f. prakt. Chem. II. 66 (1902), 481 to 516.

somewhat lower than that of geraniol, but it does not combine with calcium chloride, hence can be separated from geraniol by his means. Its diphenyl urethane, however, does not melt at '3 to 75° as stated by Hesse and Zeitschel, but at 52 to 53°. Nerol is contained in the oil both free and as acetate. For its properties see vol. I, p. 362.

Geraniol was first found in the oil by Tiemann and Semmler, but ts presence was first definitely established by Hesse and Zeitschel vho oxidized it to citral (m. p. of citrylidene cyanacetic acid 122').

Jasmone. The presence in neroli oil of this ketone, first found y A. Hesse[1]) in jasmin oil, is probable, since the corresponding raction yielded a semicarbazone melting at 200 to 204°[2]).

Nerolidol. As found by Hesse and Zeitschel, the high boiling ractions contain a hitherto unknown sesquiterpene alcohol $C_{15}H_{26}O$, nerolidol (comp. vol. I, p. 399). It is identical with eruviol and is characterized by a phenyl urethane melting at 7 to 38°, the formation of which, however, requires several veeks' standing of the alcohol with the reagent[3]).

Farnesol, which has a still higher boiling point than nerolidol, vas isolated by Schimmel & Co.[3]) by treating fraction 127" (4 to mm.) with phthalic acid anhydride. It was identified by means f its constants and by its conversion into farnesal (m. p. of emicarbazone 127 to 132° in place of 133 to 135°)[4]).

Paraffin. The stearoptene of orange flower oil, also known s neroli camphor or *aurade*, was first found by Boullay[5]). It s a paraffin which occurs in almost all flower oils and, when ure, is completely odorless and tasteless. It melts at 55°[6]).

Acids. In addition to the *acetic acid* already mentioned, eroli oil contains *phenyl acetic acid*[7])[8]) which is found in larger

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[1]) Berl. Berichte 32 (1899), 2619.

[2]) Report of Schimmel & Co. April 1903, 55.

[3]) *Ibidem* 1914, 72.

[4]) Comp. M. Kerschbaum, Berl. Berichte 46 (1913), 1732.

[5]) Journ. de Pharm. 14 (1828), 497.   Trommsdorff's Neues Journ. der harm. 19, I. (1829), 227.

[6]) Flückiger and Hanbury, Pharmacographia. II. edition. London 1879, . 127. — E. and H. Erdmann, Berl. Berichte 32 (1899), 1214, footnote.

[7]) Hesse and Zeitschel, Journ. f. prakt. Chem. II. 66 (1912), 481 to 516.

[8]) Report of Schimmel & Co. October 1902, 54 to 58. — Journ. f. prakt. hem. II. 67 (1903), 315 to 325.

FAMILY: RUTACEÆ.

amounts in the oil shaken out of the aqueous distillate, *benzoic acid*[1]), also traces of *palmitic acid*[2]). All of these acids presumably exist in the oil as esters.

Phenols are present, but only in traces[3]).

Anthranilic acid methyl ester. The most important role in the formation of the orange flower perfume is played by the small amount of *anthranilic acid methyl ester,* which was found in the oil in 1894 in the laboratory of Schimmel & Co.[3]). It is the presence of this substance that causes the fluorescence of the oil.

Anthranilic acid methyl ester $NH_2 \cdot C_6H_4 \cdot COOCH_3$ boils at 132° under 14 mm. pressure, melts at 25° and while in the liquid condition at 15° has a specific gravity of 1.168. In the undiluted condition its odor is unpleasant. Only when greatly diluted does its odor remind of the fragrance of orange blossoms.

Several weeks after the *Bericht* of Schimmel & Co. and with it the report of Walbaum had been issued, there was published a paper by E. and H. Erdmann[4]) who claimed the scientific priority of the discovery of the ester in neroli oil.

After a rejoinder by H. Walbaum[5]), E. and H. Erdmann[6]) claimed to prove their scientific priority by a German application for letters patent, E. 5958, in which the occurrence of anthranilic acid methyl ester in neroli oil is mentioned without, however, producing analytical proof. These letters patent were published July 5, 1900, hence *15 months after* the publication of H. Walbaum's first report. It thus becomes apparent that H. Walbaum's

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[1]) Report of Schimmel & Co. October 1902, 54 to 58. — Journ. f. prakt. Chem. II. 67 (1903), 315 to 325.

[2]) Hesse and Zeitschel, Journ. f. prakt. Chem. II. 66 (1912), 481 to 516.

[3]) Report of Schimmel & Co. April 1899, 32. — H. Walbaum, Journ. f. prakt. Chem. II. 59 (1899), 350.

[4]) Berl. Berichte 32 (1899), 1213.

[5]) *Ibidem* 32 (1899), 1512.

[6]) *Ibidem* 33 (1900), 2061. In a footnote, E. and H. Erdmann accuse me of having wilfully ignored their paper on neroli oil in the first edition of this work. This contribution, which I am supposed to have ignored, appeared in the number of the *Berl. Berichte* which was issued May 15, 1899. However, the final correction of form 40 of the first edition was returned to the printer May 4, 1899 and the final form had been printed May 14. It was impossible, therefore, to take notice of their paper which came to my attention a few days later. This I regretted very much, for otherwise I might have been in a position at that time to refute the unwarranted claims made by the Erdmanns.

report was made public sooner than any of the communications
by the Messrs. Erdmann.

Indol, likewise an important constituent of the oil, was first
found by P. Engels[1]) in neroli pomade, later by Hesse and
Zeitschel in the oil itself.

Pyrrol and pyrrol derivatives, found by H. and E. Erdmann[2])
in neroli oil, do not, according to Schimmel & Co.[3]) and Hesse
and Zeitschel, appear to occur in genuine, unadulterated neroli
oil.   Probably the appearance of the pyrrol reaction (cherryred
coloration of a pine shaving moistened with hydrochloric acid
when exposed to the vapors of the first fraction) may be attri-
buted to an adulteration with petitgrain oil.

At the close of their second contribution on neroli oil, Hesse and
Zeitschel presented a compilation of the constituents of the oil with
approximate amounts. In somewhat modified form, in which the
more recent investigations are considered, it is herewith reproduced.

<div align="center">Composition of Neroli oil.</div>

Constituents.		approximate amount in p.c.
Hydrocarbons 35 p.c.	1. Pinene	35 p.c.
	2. Camphene	
	3. Dipentene	
	4. Paraffin C$_{?}$	
Terpene alcohols and their acetates 47 p.c.	5. *l*-Linalool	30 p.c.
	6. *l*-Linalyl acetate . . . . ·.	7 p.c.
	7. *d*-Terpineol	2 p.c.
	8. and 9. Geraniol ; Nerol	4 p.c.
	10. and 11. Geranyl acetate · Neryl acetate	4 p.c
Sesquiterpene derivatives 6 p.c.	12. *d*-Nerolidol	6 p.c.
Nitrogenous com- pounds 0.7 p.c.	13. Anthranilic acid methyl ester	0.6 p.c.
	14. Indol	less than 0.1 p.c.
Acids and phenols 0.1 p.c.	15. Acetic acid	--
	16. Palmitic acid . . . . ·	
Other constituents, resinous products and loss ·	Decylic aldehyde (?) and esters of phenyl- acetic acid and benzoic acid, jasmone and farnesol	11.2 p.c.

In the orange blossom *water* oil all of the above mentioned
constituents are likewise found, but in different ratios. Those

[1]) Journ. f. prakt. Chem. II. 66 (1902), 504.
[2]) Berl. Berichte 32 (1899), 1217.
[3]) Report of Schimmel & Co. October 1902, 54.

substances which are more soluble in water, such as the alcohols'
and anthranilic acid methyl ester, exist in larger percentage in
the water oil than in the neroli oil. The more difficultly soluble
constituents, such as the esters of the terpene alcohols, are present
in smaller amounts. The water oil possibly also contains *phenyl
acetonitrile,* likewise a nitrogenous substance melting at 159°[1]).

The orange blossom *extract* oil, according to Schimmel & Co.[2])
contains, in addition to the substances found in the distilled oil,
the following substances: traces of benzaldehyde (m. p. of semi-
carbazone 214"); a basic substance, with a decided odor of
nicotine, that boils above 110° (6 mm.); and a nitrogenous sub-
stance which, upon saponification of the oil, is hydrolyzed to
ammonia and phenyl acetic acid and which, in all probability,
may be regarded as the *nitrile of phenyl acetic acid.* The
nitrogenous substance melting at 159° which had been found by
Hesse and Zeitschel in the water oil, has also been obtained
from the extract oil. Finally, it contains a ketone with the odor of
jasmine, presumably jasmone (m. p. of semicarbazone 204 to 205°).

Examination. The most common and most dangerous
adulterants are bergamot oil and petitgrain oil. Inasmuch as
both of these oils, like neroli oil, contain as principal consti-
tuents linalool and linalyl acetate, their detection in small amounts
is impossible. Larger additions result in an increase of the specific
gravity and ester content. The latter in the case of pure neroli
oil fluctuates between 7 and 24 p.c. (S.V. 20 to 69), in the case
of bergamot between 34 and 45 p.c. (S.V. 97 to 130), and in
the case of petitgrain oil between 37 and 57 p.c. (S.V. 106 to
163). Orange flower oils, the saponification value of which is
higher than 70, should be rejected as suspicious.   ·

Not infrequently, however, mixtures of more or less saponified
petitgrain, bergamot and orange oils are added to the flowers
previous to their distillation. In such an instance the identi-
fication of limonene can be taken as proof of adulteration.

The property of neroli oil to separate paraffin when subjected
to a freezing mixture, has been utilized as a test. This is justifiable
in so far as the addition of paraffin-free oils may reduce the relative.

[1]) Hesse and Zeitschel, *loc. cit.*
[2]) Report of Schimmel & Co. October 1903, 49.

paraffin content to such an extent that it no longer separates in a freezing mixture. It should be remembered, however, that un-adulterated oils may, at times, be poor in paraffin. If at the time of the flower harvest, a large amount of material must be handled rapidly, it may occur that the distillation is not carried to exhaustion hence less of the difficultly volatile paraffin passes over into the oil than usual. Moreover, dependence is placed upon comparison of the physical constants with those of good oils, also on the sense of smell.

432. Oil of Neroli Portugal.

Oleum Aurantii florum dulce. — Süßes Orangenblütenöl. — Essence de Néroli Portugal.

Origin. Oil of sweet orange blossoms, Neroli Portugal, *i. e.* the oil distilled from the flowers of the sweet orange, is rarely met in the pure state in commerce. The oil sold under the above designation is almost invariably a mixture of different aurantiaceous oils.

Properties. For scientific purposes an oil was prepared by E. Theulier[1]) in southern France. The oil obtained by simple distillation without cohobation was dark yellow in color. Its odor did not remind of that of ordinary neroli oil. Its specific gravity was 0.860 at 23°, its angle of rotation ¡ 29°30′, the ester content 6.35 p. c. With 90 p. c. alcohol the oil produced a silky turbidity. In the cold it separated paraffin melting at 55°.

An oil sent to Schimmel & Co.[2]) from southern France had the following properties: $d_{15°}$ 0.8686; $\alpha_D + 45°16'$; $n_{D 20°}$ 1.47352; A. V. 1.8; E. V. 16.7; soluble in 0.5 vol. of 90 p. c. alcohol, the addition of more than 5 vol. produced opalescence.

An oil[3]) distilled in Germany from the fresh flowers of the Spanish sweet orange, *Citrus Aurantium,* Risso, possessed very different properties. The shipment of the flowers had been made in iron cylinders from which the air had been exhausted after filling. A yield of 0.154 p. c. of oil was obtained with a specific gravity of 0.893 at 15° and an optical rotation $\alpha_D + 16°8'$.

An oil[4]) distilled in Spain revealed the following properties: $d_{15°}$ 0.8571; $\alpha_D + 42°47'$; $n_{D 20°}$ 1.47274; A. V. 1.6; E. V. 6.8; in-

[1]) Bull. Soc. chim. III. 27 (1902), 278.
[2]) Report of Schimmel & Co. April 1910, 79.
[3]) Bericht von Schimmel & Co. October 1889, 38.
[4]) Report of Schimmel & Co. October 1903, 77.

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soluble in 80 p.c. alcohol, readily soluble in 90 p.c. alcohol with fluorescence and the separation of traces of paraffin.

Another oil from the same source examined by Schimmel & Co. had the following properties: $d_{15°}$ 0.8746; α_{D} + 43°22'; n_{D20} 1.47450; A. V. 3.7; E. V. 16.7; insoluble in 10 vol. of 80 p.c. alcohol, soluble in 0.3 vol. of 90 p.c. alcohol, from 2.5 vol. on opalescence is produced.

The properties of an Algerian oil are recorded by A. Chapus [1]): $d_{15°}$ 0.8731; α_{D} + 26°15'; ester content, computed as linalyl acetate, 34.18 p.c.

Composition. The oil examined by Theulier [2]) boiled between 160 and 233° and appeared to contain appreciable amounts of the higher terpenes. d-*Camphene* was identified by means of *iso*-borneol melting at 212 , *limonene* by means of its tetrabromide melting at 105 , and d-*linalool* by means of Doebner's compound of citral melting at 198.5° which had been obtained upon oxidation of the linalool fraction. Those portions of the oil boiling above linalool were not examined. Anthranilic acid methyl ester was not contained in the oil. However, this ester was found to the extent of 0.3 p.c. in a Spanish oil and was identified by means of its benzoyl derivative (m. p. 100 to 102°) and by means of its picrate (m. p. 105 to 106°).

433. Oil of Sweet Orange Leaves.

Two oils distilled in southern France from the leaves of the sweet orange tree (petitgrain Portugal) had the following properties [3]): d_{15} 0.8602 and 0.8584; α_{D} + 56°46' and + 53°52'. An Algerian oil was examined with the following results [4]): $d_{15°}$ 0.8705; α_{D} + 21°33'; ester content, computed as linalyl acetate 21.6 p.c. The oil contains [5]) d-*camphene* (m.p. of *iso*borneol 212°), *limonene* (m.p. of tetrabromide 104°), *linalool* (?), *citral*, about 4 p.c. (m.p. of naphthocinchoninic acid 197°) and *geraniol*, about 12 p.c. (calcium chloride compound).

[1]) Journ. de Pharm. et Chim. VI. 30 (1909), 484.
[2]) Bull. Soc. chim. III. 27 (1902), 278.
[3]) Berichte von Roure-Bertrand Fils October 1904, 35 and October 1910, 42.
[4]) A. Chapus, Journ. de Pharm. et Chim. VI. 30 (1909), 484.
[5]) G. Litterer, Bull. Soc. chim. III. 33 (1905), 1079.

434. Oil of Petitgrain.

Oleum Petitgrain. — Petitgrainöl. — Essence de Petitgrain.

Origin and Production. Petitgrain oil is obtained by steam distillation from the leaves and twigs of the bitter orange, *Citrus Bigaradia*, Risso. At times the fruits adhering to the branches are distilled along. Formerly the oil was produced principally in southern France. In Paraguay the distillation was introduced by the French botanist Balanza who went to that country in 1873. The quality of this oil, at first poor, was improved in the course of years. On account of its greater reliability and uniformity it is now generally preferred to the French oil which is frequently adulterated.

In southern France the leaves and twigs which result from the pruning of the bitter orange tree are commonly distilled[1]).

According to the reports from Paraguay the most ruinous methods are being employed which have resulted in complete annihilation of the underbrush of orange trees or *Manchones* over wide areas[2]). In his book *Paraguay in Wort und Bild*, R. von Fischer-Treuenfeld renders the following account[2])[3]).

"Although wild orange groves are still numerous, they are, because of the pernicious methods practiced, remote from the inhabited places. The harvest is carried on all year, but principally from October to April. About 5 cm. above the ground the trees are chopped down. The leaves and young fruits are distilled on the spot, the wood being used as fuel. Thus indolence and vandalism have led to the annihilation of the orange forests. More recently the Government has endeavored to prevent the chopping down of the trees and to regulate the harvesting by law. Hence the price of the oil has risen and it is more and more difficult to obtain the product".

The number of distilleries producing petitgrain oil in 1909 was estimated at 30[4]) located as follows: 20 in Jaguaron[5]), 4 in Ita, 3 in San José de la Cordillera, 1 in Itacuruby and 2 in Nemby.

[1]) L. Mazuyer, Americ. Perfumer 4 (1909), 106, 127.

[2]) Report of Schimmel & Co. April 1902, 55.

[3]) II. ed. Berlin 1906, p. 187.

[4]) Le Messager de Sao Paolo for 9. 7. 1909; Report of Schimmel & Co. April 1910, 89.

[5]) Comp. also Chemist and Druggist 51 (1897), 110.

Collectively they had a capacity of from 2600 to 3000 kg. monthly or about 36000 kg. annually. Asuncion is the market for petitgrain oil.

The factories are of very simple construction. The site is located near a creek flowing through the orange grove. The hut is covered with palm leaves. The apparatus consists of a boiler fired with wood and in which the pressure does not exceed one atmosphere, a large still for the plant material, a serpentine condenser, and Florentine flasks used as receivers. The distillation lasts 36 hours and the yield amounts to 0.33 to 0.4 p.c.[1]). The daily output amounts to from 3 to 4 l. of oil which is transferred to tin containers that are sealed immediately and transported.

The export of petitgrain oil from Paraguay is indicated by the following figures: —

1899[2])	1900[2])	1901[2])	1902[2])	1903[2])
6106 kg.	9545 kg.	17834 kg.	19436 kg.	25176 kg.

Value: -ℳ 48848.- -ℳ 76360.— -ℳ 107000.- -ℳ 116616.— -ℳ 146531.—

1906[3])	1907[3])	1908[4])	1909[4])
9698 kg.	10872 kg.	30274 kg.	31000 kg.

Properties. The odor of Paraguay petitgrain oil resembles that of neroli oil, but is much less delicate; its taste is aromatic and somewhat bitter; the color yellowish. d_{15} 0.886 to 0.900; α_0 +5 to −2°45'; n_{D20} 1.459 to 1.464; A. V. up to 2; E. V. 106 to 163 · 37 to 57 p.c. linalyl acetate. Soluble in 1 to 1.5 vol. and more of 80 p.c. alcohol, the dilute solution being occasionally opalescent. Most of the oils are also soluble in 2 to 4 vol. of 70 p.c. alcohol, though frequently with opalescence and even turbidity.

Those oils with a lower specific gravity and a larger dextrorotation are mostly poorer in linalyl acetate and hence inferior[2]). Nevertheless, oils have been frequently observed which, in spite of the deviations mentioned, revealed a normal ester content. Thus for oils with from 37 to 46 p.c. linalyl acetate content,

[1]) E. Charabot and L. Pillet (Bull. Soc. chim. III. 19 [1898], 853; 21 [1899], 74) report much lower yields. They obtained only from 0.133 to 0.184 p.c.

[2]) v. Fischer-Treuenfeld *loc. cit.* p. 304.

[3]) Report of Schimmel & Co. October 1909, 101.

[4]) *Ibidem* October 1910, 106.

[5]) *Ibidem* October 1910, 107.

the following constants have been observed: d_{1n} as low as 0.883; and $\alpha_{D} + 5°10'$ to $+ 11°3'$. In isolated cases the oils differed from the normal only by a stronger dextrorotation (e. g. d_{1n} 0.8907; $\alpha_{D} + 7°48'$; 39.7 p.c. ester; yielded a turbid solution with about 5 vol. and more of 70 p.c. alcohol, soluble in 1 vol. and more of 80 p.c. alcohol.) Presumably these deviations are due to the selection of the crude material, though unfavorable climatic conditions may be accountable therefor.

Eight petitgrain oils distilled by E. Charabot and L. Pillet[1]) in Cannes from the leaves of the bitter orange had the following properties: d_{1n} 0.8910 to 0.8937; $\alpha_{D} - 4°45'$ to $- 6°15'$; soluble in 1 vol. of 80 p.c. alcohol; ester content from 51.5 to 69.6 p.c.

For an oil distilled by themselves Roure-Bertrand Fils[2]) found: d_{1n} 0.8980; $\alpha_{D} - 4°20'$; S. V. 161.4; E. V. after acetylation 203.0; soluble in 3.5 vol. of 70 p.c. alcohol.

Properties of Petitgrain oils of various Sources.

Source	d_{1n^o}	α_{D}	A. V.	E. V.	p.c. Ester
Calabria . . .	0.8746	+ 18"	0.5	75.4	26.3
Spain	0.8849	+ 8°25'		81.7	28.6
Comores	0.8664	+ 42°45'	1.8	31.0	10.9
Jamaica[3]) . . .	0.8846	6°30'	--	82.0	28.7
West Indies . . .	0.8531	-+ 43°36'	1.2	6.1 ·	2.1
South America[4]) .	0.887	+ 2"	-	—	36.5
Syria[5])	0.8857	3°24'	--		27.1

[1]) Bull. Soc. chim. III. 19 (1898), 853; 21 (1899), 74.

[2]) Berichte von Roure-Bertrand Fils, October 1910, 42.

[3]) This is apparently the same oil on which the Imperial Institute of London (Bull. Imp. Inst. 11 [1913], 437) reports and which had the following constants: d_{1n} 0,8884; $\alpha_{D} - 6°45'$; soluble in 1 vol. and more of 80 p.c. alcohol. It contained 31,6 p.c. free and 55,65 p.c. esterified alcohols. Schimmel & Co. (Report April 1914, 83) express themselves in the following words: "The oil is noteworthy for its comparatively high degree of lævo-rotation, for in case of the commercial oil, which comes mostly from Paraguay, the rotation varies from -+ 5° to $- 2°43'$. It is possible that this may be due to the circumstance that the crude material consisted principally of leaves, at any rate experiments made many years ago by Charabot and Pillet (Bull. Soc. chim. III. 21 [1899], 74) showed that the leaves of the bitter orange tree yielded oils which were more lævorotatory than the other oils."

[4]) J. C. Umney and C. T. Bennett, Pharmaceutical Journ. 72 (1904), 217.

[5]) Berichte von Roure-Bertrand Fils April 1911, 26.

The influence of climatic conditions on the formation and composition of petitgrain oils has been studied by Jeancard and Satie[1]) for the years 1901 to 1903.

Composition. *Pyrrol* and *furfurol.* The vapors of the first distillate of the oil color a pine shaving, moistened with hydrochloric acid, cherry-red[2]), a reaction that indicates the presence of *pyrrol* derivatives[3]). Besides the lowest fraction contains *furfurol* (color reaction with aniline hydrochloride[3]).

Camphene. When fraction 160 to 170° was treated with glacial acetic acid-sulphuric acid, the odor of *iso*borneol resulted. However, no crystals of this alcohol could be obtained[4]).

β-Pinene. Upon oxidation of fraction 167 to 170 ($d_{15°}$ 0.8474; a_D — 7 10') with potassium permanganate in alkaline solution, a good yield of sodium nopinate, crystallizing in shining laminæ, was obtained. Decomposed with sulphuric acid, it yielded nopinic acid melting at 126 to 127°. For further identification nopinic acid was converted into nopinone which condensed readily with benzaldehyde forming the benzylidene compound $C_9H_{12}O : CHC_6H_5$, melting at 107°[5]).

Dipentene and *Limonene.* Walbaum and Hüthig[4]) proved the presence of dipentene by means of its tetrabromide (m. p. 125°), whereas, according to F. Tiemann and F. W. Semmler[6]), limonene is contained in the oil. E. Charabot and L. Pillet[7]) have found that the petitgrain oil distilled from the leaves only contains no limonene and that the *d*-limonene occasionally found in the oil is due to the small fruits.

l-*Linalool*, which occurs both free and as ester, was first shown to be present by Tiemann and Semmler. This observation was later verified by Walbaum and Hüthig by means of the phenylurethane of the linalool melting at 65°, a compound previously unknown.

[1]) Bull. Soc. chim. III. 29 (1903), 1089.

[2]) H. and E. Erdmann, Berl. Berichte 32 (1899), 1217.

[3]) Report of Schimmel & Co. October 1902, 69.

[4]) H. Walbaum and O. Hüthig, Journ. f. prakt. Chem. II. 67 (1902), 321. Report of Schimmel & Co. October 1902, 69.

[5]) Report of Schimmel & Co. April 1914, 83.

[6]) Berl. Berichte 25 (1892), 1186.

[7]) Bull. Soc. chim. III. 21 (1899), 74.

d-*α-Terpineol*. (m. p. 34°; m. p. of phenylurethane 112°[1]).)

Nerol. H. von Soden and O. Zeitschel[2]) found about 2 p.c. of this alcohol in petitgrain oil.

Geraniol is present both free and as acetate[3]); m. p. of diphenyl-urethane 82°; analysis af the silver salt of the acid[4]).

The highest boiling portions of petitgrain oil contain sesquiterpenes[5]) that have not been farther investigated. The blue fluorescence of the oil is in all probability due to anthranilic acid methyl ester[5]). Upon shaking the fraction which boils in the neighborhood of 200° with dilute sulphuric acid, Walbaum and Hüthig obtained traces of an oil which had a strongly basic odor and which probably produces the characteristic petitgrain odor.

Adulteration and Examination. Petitgrain oil is adulterated with orange oil, lemon oil and turpentine oil[6]). These additions are readily recognized by the lowering of the specific gravity, lowering of the saponification value and of the solubility, and finally by the change in the angle of rotation.

Of other adulterants that are more difficult of detection, the following have been observed: ethyl tartrate[7]), oleic acid[7]), also terpinyl acetate[8]).

435. Oil from Immature Oranges.

From the unripe bitter Sicilian orange, H. Haensel[9]) obtained upon distillation 0.712 p.c. of oil ($α_D$ about + 49°), and from Spanish material 0.372 p.c. ($α_D$ about + 58°). This oil contains appreciable amounts of a *pyrrol* derivative, for the vapors, even

[1]) H. Walbaum and O. Hüthig. Journ. f. prakt. Chem. II. 67 (1902), 321. Report of Schimmel & Co. October 1902, 69.

[2]) Berl. Berichte 36 (1903), 265. -- Comp. also Report of Schimmel & Co. April 1903, 62.

[3]) J. Passy, Bull. Soc. chim. III. 17 (1897), 519.

[4]) Berl. Berichte 25 (1892), 1186.

[5]) Report of Schimmel & Co. October 1902, 68.

[6]) Comp. *Ibidem* April 1908, 78.

[7]) E. J. Parry, Chemist and Druggist 75 (1909), 410.

[8]) Report of Schimmel & Co. October 1912, 92. For the detection of terpinyl acetate, see Bergamot oil, p. 68.

[9]) Pharm. Ztg. 51 (1906), 352.

of the unfractionated oil, produce a bluish-red color on a pine shaving moistened with hydrochloric acid[1]). The principal constituent of the oil is *limonene*[2]).

436. Oil of Citrus Hystrix.

OIL FROM THE FRUIT RINDS. In Buitenzorg 4 p.c. of an oil were obtained upon distillation of the fruit rinds of *Djeroek pœroet* (*Citrus Hystrix*, D.C.; *C. Papedia*, Miq.). $d_{26°}$ 0.942; $+9°$. It contained 40 p.c. of *citral*[3]).

A sample which had been presented to Schimmel & Co. by Dr. de Jong, of Buitenzorg, was apparently identical with this oil, but in the meantime it had strongly resinified, as also became apparent from the high specific gravity: $d_{15°}$ 0.9654; $\alpha_D + 7°18'$; $n_{D20°}$ 1.48277; soluble in 1 vol. and more of 80 p.c. alcohol. The light yellow oil had a lemon-like odor.

OIL FROM THE LEAVES. According to B. T. Brooks[4]), the leaves do not yield more than 0.08 p.c. of volatile oil with the following properties: $d_{30°}^{30°}$ 0.9150; $\alpha_D - 10.50°$; $n_{D30°}$ 1.4650; S.V. 50.2. Its odor resembles that of the oil from grape fruit.

437. Oil of Citrus trifoliata.

A Chinese neroli oil, said to have been obtained from the leaves of *Citrus trifoliata*, L. (*C. triptera*, Desf.; *Ægle sepiaria*, D.C.) has been described by J. C. Umney and C. T. Bennett.[5])

The yellowish-brown oil had a peculiar sweetish odor, revealed a very faint blue fluorescence and had the following constants: $d_{15°}$ 0.850; $\alpha_D + 35°$; ester content 4.97 p.c., computed as linalyl acetate; total alcohol content 25.17 p.c., computed as linalool. According to the investigators the oil contains *limonene, camphene, linalool, linalyl acetate, anthranilic acid methyl ester* and a *paraffin*. How these substances were identified is not stated.

[1]) E. and H. Erdmann, Berl. Berichte 32 (1899). 1217.

[2]) Pharm. Ztg. 51 (1906), 352.

[3]) Jaarb. dep. Landb. in Ned.-Indië, Batavia 1909, 64; Report of Schimmel & Co. April 1911, 51.

[4]) Philippine Journ. of Sc. 6 (1911), A, 349.

[5]) Pharmaceutical Journ. 69 (1902), 146.

438. Oil of Citrus reticulata.

According to Brooks[1]) an oil can be obtained in the Philippines from the rind of the fruit of *Citrus reticulata,* Blanco, known there as *Naranjita,* which is almost identical with Italian oil of orange. *Citrus reticulata* is commonly regarded as synonymous with *C. Aurantium,* L., but, according to Brooks, this assumption is not correct. The oil expressed from the green rinds had the following properties: $\alpha_{D30°}$ 90.85° (+?); $n_{D30°}$ 1.4700; E.V. 8.0; evaporation residue 2.25 to 2.4 p.c. It contained about 92 p.c. of *limonene,* about 0.3 p.c. of a wax-like *stearoptene* melting at 116 to 117°, 0.5 p.c. of an *acid* (possibly butyric or caprylic acid), also traces of a *phenol.*

Another species of *Citrus* cultivated in the Philippines is the *Citrus Aurantium* Blanco (possibly synonymous with *C. Aurantium,* L.), the fruits of which are called *Cajel.* These are not suitable for the production of oil, the yield being too small. Its properties are: $d_{30°}^{30°}$ 0.8390; n_D 1.4675; S.V. 8.5.

The botanical position of both species remains to be determined more accurately.

439. Oil of West Indian Sandal Wood.

Oleum Santali ex India occidentali. - Westindisches Sandelholzöl. — Essence de bois de Santal des Indes Occidentales.

Origin. Until recently the origin of West Indian sandal wood was not known. From a study of the wood and the leaves, E. M. Holmes, W. Kirkby and A. Petersen arrived at the conclusion that the plant must belong to the family *Rutaceæ* and could by no means be assigned to the family *Santalaceæ*[2]). Because of the want of flowers, nothing more definite could be established. At the suggestion of Mr. Holmes, of London, the firm of Schimmel & Co. in 1898 succeeded in obtaining flowering branches of the tree in Puerta Cabello, Venezuela, whence the wood is brought into the market. An examination by Holmes led to the conclusion that the plant belonged to the family *Rutaceæ.* He assumed it to be an unknown species and named it *Schimmelia*

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[1]) Philippine Journ. of Sc. 6 (1911), A, 345.
[2]) Pharmaceutical Journ. III. 16 (1886), 757, 821, 1065.

oleifera[1]). Later, however, he agreed with the conclusion arrived at by Dr. Urban of Berlin who determined the plant as *Amyris balsamifera*, L. The error was caused by the circumstance that the English botanists had assigned the genus *Amyris* to the family *Burseraceæ*, whereas in Germany it is assigned to the *Rutaceæ*, which is regarded as quite correct by Holmes. Inasmuch as in English botanical literature no botanical description of a rutaceous plant corresponded to the West Indian plant, Holmes regarded it as a new species.

The wood, which in no way resembles East Indian sandal wood, consists of club-like pieces varying in thickness from that of a thumb to that of an arm. It is white and hard and is covered with a gray bark. The anatomical structure of the wood has been studied and described by Petersen and Kirkby.[2])

Upon distillation the well comminuted wood yields 1.5 to 3.5 p.c. of oil.

Properties. The viscid oil has but a faint, not very pleasant odor. $d_{15°}$ 0.950 to 0.970; $\alpha_D + 19$ to $+29°$, rarely lower; $n_{D20°}$ 1.508 to 1.513; A.V. up to 3.0; E.V. up to 6.0; E.V. after acetylation 66 to 125, corresponding to from 27 to 55 p.c. of amyrol, $C_{15}H_{26}O$. The saponification of the acetylated oil must be effected with a large excess of alkali and must be continued for 2 hours, since a shorter period yields incorrect results. Soluble in 1 vol. or even less of 90 p.c. alcohol, occasionally in 2 to 10 vol. of 80 p.c. alcohol.

Composition. After boiling the oil with acetic acid anhydride, W. Dulière[3]) had obtained a saponification value corresponding to 41.93 p.c. of an alcohol $C_{15}H_{26}O$. Thereupon H. von Soden[4]) isolated the alcohol and named it amyrol. It is an almost colorless, viscid liquid which forms a clear solution with 3 to $3^1/_2$ parts of 70 p.c. alcohol. $d_{15°}$ 0.980 to 0.982; $\alpha_D + 27°$; boiling point 299 to 301° under 748 mm. pressure, 151 to 152° under 11 mm. pressure.

With phthalic acid anhydride amyrol cannot be esterified, since it is dehydrated, neither is the acetylation quantitative.

[1]) Pharmaceutical Journ. III. 62 (1899), 53, 137, 205.
[2]) *Ibidem* 16 (1886), 757, 821, 1065.
[3]) Bull. de l'académie roy. de méd. de Belgique IV. 11 (1897), 768.
[4]) Pharm. Ztg. 45 (1900), 229.

Later H. von Soden and W. Rojahn[1]) found that amyrol is no definite chemical substance but that, upon repeated fractionation, it can be resolved into several alcohols. The higher boiling substance, which predominates, has a faint, peculiar, aromatic odor and, according to elementary analysis, the composition $C_{15}H_{25}OH$. d_{15}, about 0.987; α_{D}, about $+ 36°$; b.p. 299°. Mineral acids and other dehydrating agents convert it into a sesquiterpene $C_{15}H_{24}$. The lower boiling alcohol appears to have the composition $C_{15}H_{26}OH$ and is optically inactive.

The alkaline saponification liquid, when acidulated with sulphuric acid, yielded an oil which crystallized in part and which had a strong odor of acetic acid. In order to remove the acid it was shaken with a solution of sodium carbonate. The remaining crystals, after recrystallization from methyl alcohol, melted at 117. This substance, named *amyrolin,* is free from nitrogen, contains no methoxy groups and has the composition $C_{14}H_{12}O_{3}$. In alcoholic potassa, amyrolin is soluble with a yellowish-green fluorescence. It adds bromine yielding an amorphous, white dibromide melting at 157 to 159°. Judging from its behavior, amyrolin appears to be a lactone of the aromatic series.

According to E. Deussen[2]), West Indian sandalwood oil contains *d*-cadinene, which yielded a hydrochloride melting at 117 to 118°. When hydrogen chloride was split off, l-*cadinene* resulted. Whether *d*-cadinene is really contained in the original oil has not been proven beyond question by Deussen.

In the lower boiling fractions (137 to 139° under 17 mm. pressure; d_{15} 0.9125; $\alpha_{D} + 7$°) E. Deussen[3]) demonstrated the presence of *β-caryophyllene* (m. p. of nitroso-*β*-caryophyllene 156 to 157°). In one instance the sesquiterpene content of a West Indian sandalwood oil was estimated at 30 to 40 p.c., of which 16 to 17 p.c. was cadinene. In the distillation residue a substance $(C_{21}H_{30}O)_{3}$ was found[3]).

The aqueous distillate contains *methyl alcohol, diacetyl* and *furfurol*[4]).

[1]) Pharm. Ztg. 45 (1900), 878.
[2]) Arch. der Pharm. 238 (1900), 149; 240 (1902), 288.
[3]) Liebig's Annalen 388 (1912), 144.
[4]) Report of Schimmel & Co. April 1908, 73.

440. Yucatan Elemi Oil.

Yucatan elemi is supposed to be derived from *Amyris ele-mifera* (L.), Royle *(A. Plumieri,* D.C., family *Rutaceæ).*

Upon distillation the oleoresin yielded 8 to 10 p.c. of volatile oil, $d_{15°}$ 0.945. The bulk of the oil distilled between 175 and 180° [1]).

Family: BURSERACEÆ.

441. Oil of Myrrh.

Oleum Myrrhæ. — Myrrhenöl. — Essence de Myrrhe.

Myrrh consists of the air dried juice, occurring, originally as emulsion in the bark parenchyma, of several species of the genus *Commiphora* of the family *Burseraceæ.* These shrubs grow wild in part and in part are cultivated in the countries bordering on the Red Sea[2]), more particularly along the Somali coast of East Africa[3]). They also flourish in parts of Arabia and of Persia.

As to the numerous commercial varieties and their botanical origin, opinion is decidedly divided. Individual investigators enume-rate a number of species[4]) as botanical source.

The numerous varieties differ considerably on account of their botanical origin and geographic source. The volatile oils from two of these, *viz.,* the Heerabol and the Bisabol myrrh have been described.

HEERABOL MYRRH OIL.

Origin. The Heerabol myrrh, official in the German Pharma-copoeia, is obtained from southern Arabia and the coast regions of Somaliland. In his *"Die Harze und Harzbehälter"*, 2nd ed., Leipzig 1906, p. 891, Tschirch makes the following statement: "I am of the opinion that it is too early to assign a definite

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[1]) A. Tschirch and J. Cremer, Arch. der Pharm. 240 (1902), 316.

[2]) E. Meyer, *Botanische Erläuterungen zu Strabons Geographie.* Königs-berg 1852, p. 139.

[3]) Dymock, Materia medica of Western India. Bombay 1885, p. 155.

[4]) A. Engler, *Syllabus der Pflanzenfamilien, V. Aufl.,* Berlin 1907, p. 151. — Engler-Prantl, *Die natürlichen Pflahzenfamilien, III. Teil, 4. Abt.,* p. 255. — G. Schweinfurth, Berichte d. deutsch. pharm. Ges. 3 (1893), 237. — E. M. Holmes, Pharmaceutical Journ. 61 (1898), 547; 76 (1906), 254; 91 (1913), 116.

species. This much only is true that a *Commiphora* species of northern Africa yields the drug." In another place (p. 394) he writes that of the several species *C. Myrrha* (Nees) Engler var. *Molmol*, Engler is more probably the parent plant than any other.

Heerabol myrrh may be distinguished from other varieties in this that its petroleum ether extract, when treated with bromine vapors, becomes turbid due to a violet flocculent precipitate and the solution itself is colored red. This color reaction is likewise peculiar to the volatile oil[1]) of which the drug yields 2.5 to 10 p.c. on destillation.

Properties. Myrrh oil of commerce is viscid, its color is yellowish to greenish or brownish, its odor is that of myrrh. d_{15° 0.988 to 1.024; α_{D} — 31 to — 93°; n_{D20° 1.5197 to 1.5274; A. V. 0.8 to 6; E. V. 16 to 40; E. V. after acetylation 32 to 65; soluble in about 8 to 10 vol. or more of 90 p.c. alcohol.

Composition. An elementary analysis made by Ruickholdt which yielded results corresponding approximately with $C_{10}H_{14}O$, caused Flückiger[2]) to test the oil for carvone. The result, however, was a negative one.

Later K. Lewinsohn[3]) examined three commercial oils and an oil distilled by himself from Heerabol myrrh[1]), in which he found a number of constituents.

Cuminic aldehyde, $C_{10}H_{12}O$ (up to 1 p.c.), b. p. 116° (12 mm.); m.p. of oxime 56°; m.p. of semicarbazone 201°. Oxidation with permanganate yielded cuminic acid, $C_{10}H_{12}O_2$, m.p. 114 to 115°.

Of acids the presence of *acetic* and *palmitic acids* (m.p. 62°) only was definitely proven. In old oils both acids are found free whereas in freshly distilled myrrh oils they occur as esters.

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[1]) Older literature: Brandes, *Buchholz' Taschenbuch für Scheidekünstler und Apotheker* 1819, 125. Braconnot, Journ. de Pharm. II. 15 (1829), 288. — Bonastre, Buchner's Repert. f. d. Pharm. 34 (1830), 293. — Ruickholdt, Arch. der Pharm. 91 (1845), 10. — Bley and Diesel, *ibidem* 91 (1845), 304.

[2]) Berl. Berichte 9 (1876), 471.

[3]) Arch. der Pharm. 244 (1906), 412.

[4]) Lewinsohn suspects that in order to increase the yield, 1 p.c. of potassium hydroxide is added in the factories, to the residue after it ceases to yield oil upon distillation with water vapor and that the distillation is then continued. (Comp. A. Tschirch and W. Bergmann, Arch. der Pharm. 243 [1905], 641). In the factory of Schimmel & Co. this expediency is not resorted to.

Of *phenols* about 1 p.c. is present. In each of the four oils *eugenol* (about 0.23 p.c.; m.p. of benzoyl compound 69°) and small amounts of m-*cresol* were found.

Fractional distillation over sodium yielded four hydrocarbons (terpenes) of the formula $C_{10}H_{16}$, three of which were characterized: *pinene*[1]) (m.p. of nitrosochloride 103°; nitrolbenzylamide and nitrolpiperidide); *dipentene* (m.p. of tetrabromide 124°); *limonene* (m.p. of tetrabromide 104°); the fourth hydrocarbon ($\alpha_{D} + 80°$; m.p. of tetrabromide 115°; m.p. of monohydrochloride 6°) could not be identified.

From old oils a resin was separated by means of petroleum ether. This resin upon reduction yielded a hydrocarbon which yielded a hydrogen chloride addition product (m.p. 115 to 117°) which Lewinsohn regards as probably identical with *cadinene* dihydrochloride. The sesquiterpene boils between 163 and 168° (12 mm.); d_{20} 0.926; $\alpha_{D20°} + 22.75°$. A second sesquiterpene boiling between 151 and 154° (15 mm.); d_{21} 0.911; $\alpha_{D} + 30.4°$, could not be identified.

About the same time myrrh oil was examined by O. von Friedrichs[2]). By shaking the oil with sodium carbonate solution *formic* and *acetic* acids were isolated, likewise a non-volatile acid melting at 159°, about the nature of which nothing further was established. Apparently it is derived from an ester contained in the drug. In order to isolate phenols, the oil was shaken with 5 p.c. sodium hydroxide solution. The presence of eugenol could not be established. The bulk of the phenol mixture consisted of m-*cresol* (m.p. of tribromide 82°). With the aid of bisulphites or barium sulphanilate the presence of *cuminic aldehyde* and *cinnamic aldehyde* were established.

The oil deprived of acids, phenols and aldehydes was saponified with alcoholic potassium hydroxide. Phenol esters were not found but an acid in ester combination was isolated that crystallized in small, yellow crystals, which melted at 236°, to which

[1]) O. von Friedrichs (Arch. der Pharm. 245 [1907], 432) found no pinene in an oil examined by him, but detected it in an oil obtained from Schimmel & Co. He then draws the rash conclusion that turpentine oil had been added in the course of manufacture, which was not the case. Pinene is a normal constituent of oil of myrrh.

[2]) Arch. der Pharm. 245 (1907), 432.

the formula $C_{16}H_{21}O_3 \cdot COOH$ was assigned and which was named *myrrholic acid.*

The remaining oil, which still possessed an intense odor of myrrh, was fractionated. A colorless fraction, with an odor of turpentine, had the following constants: b. p. 130 to 136° (16 mm.); $d_{D 20°}$ 0.943; α_D — 14° 12'; $n_{D 20°}$ 1.5125; mol. refr. 64.98. Hence it appears to be a tricyclic sesquiterpene with two para bonds and one ethylene bond. It was named *heerabolene.* For a sesquiterpene of this configuration the molecular refraction of 64.45 was computed. A well crystallized bromide could not be obtained, neither a solid nitrosochloride or nitrosate. However, it yielded a crystalline hydrochloride, $C_{15}H_{24} \cdot 2HCl$ which melted at 98 to 99°.

Upon oxidation of the oil in petroleum ether solution with oxygen an amorphous substance melting at 130 to 133° was obtained. Presumably it is identical or closely related to the substance formed by autoxidation of an oil observed by Lewinsohn.

BISABOL MYRRH OIL.

Origin. Bisabol or Bissabol myrrh, also known as *Habaghadi* or *Habbak Haddi,* is obtained from the interior of Somaliland. According to Holmes it is in all probability identical with the opopanax (which see)[1] now in commerce. The parent plant of bisabol myrrh is a *Commiphora* species. According to Tschirch it is *C. erythræa,* Engler, according to Holmes *C. erythræa,* var., *glabrescens,* Engler.

Unlike Heerabol myrrh, Bisabol myrrh does not yield the bromine reaction characteristic of the former, but may be recognized by the following reaction: If 6 drops of a petroleum ether extract of Bisabol myrrh (1 : 15) is mixed with 3 cc. of glacial acetic acid, and this solution placed in a layer over 3 cc., of concentrated sulphuric acid, a rose-red color results at the zone of contact and in a short time the entire glacial acetic acid layer is colored rose-red[2]. Under like conditions, Heerabol

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[1] Although it may be assumed that the identity of Bisabol myrrh and the opopanax of this Burseracea has been well established the two oils are being treated separately in this book for the time being.

[2] Arch. der Pharm. 235 (1897), 289.

myrrh produces but a very faint rose color of the glacial·
acetic acid layer whereas the zone of contact of both layers
is green.

The volatile oil dissolved in petroleum ether (1:40) produces
the same reaction, but much more faintly. Bisabolene, however,
does not produce the color reaction.

Properties (See also opopanax oil). An oil which W. Tucholka[1])
had obtained from the resin, with a yield of 7.8 p.c., was limpid
and of light yellow color. $d_{24°}$ 0.8836; α_D — 14° 20'; it boiled
between 220 and 270°.   ·

Composition[1]).   Upon passing hydrogen chloride into the
ethereal solution of the oil, 6.5 p.c. of a hydrochloride was
obtained which melted at 79.3° and was optically active
($[\alpha]_D$ — 35° 17' in chloroform solution)[2]).   When boiled with
sodium acetate in glacial acetic acid solution it yielded a
sesquiterpene called *bisabolene.*   Later this was found in a
number of other oils (See vol. I, p. 328).

442. Opopanax Oil.

Whereas genuine opopanax[3]) is obtained from an umbelli-
ferous plant (presumably *Opopanax Chironium,* Koch), the drug
now in the market, also known as opopanax of the *Burseraceæ,*
is derived from a species of *Commiphora.*   Presumably, as
mentioned above, it is identical with Bisabol myrrh.   From it
the volatile oil is distilled.   In collections of Chinese drugs it is
commonly designated myrrh and has, no doubt, frequently been
confounded with this drug.   According to Holmes it is, indeed,
the myrrh of the Bible.

Upon distillation the opopanax of the *Burseraceæ* yields 5
to 10 p.c. of an oil of a greenish-yellow color and an agreeable,
balsamic odor.   Exposed to the air it resinifies quickly.

[1]) Arch. der Pharm. **235** (1897), 289.

[2]) On the strength of his analyses and molecular weight determinations
Tucholka supposed that he had obtained a dihydrochloride $(C_{10}H_{16}2HCl)_2$. This
assumption, however, has been proven erroneous.   Bisabolene has the formula
$C_{15}H_{24}$, hence is not a terpene but a sesquiterpene and yields a trihydro-
chloride $C_{15}H_{24}3HCl$.

[3]) Opoponax, as the word is frequently written, is less correct.

Properties. $d_{15°}$ 0.870 to 0.905; a_D — 8 to — 14°; $n_{D20°}$ 1.489 to 1.494; A. V. up to 3; E. V. 7 to 20; E. V. after acetylation 40 to 55. From 1 to 10 vol. of 90 p.c. alcohol are requisite to effect solution.

Composition. In an oil distilled by themselves, Schimmel & Co.[1]) proved the presence of *bisabolene* (See vol. I, p. 328). The hydrocarbon regenerated from its trihydrochloride (m. p. 80°) boiled between 114 and 115° (3 mm.) and, when saturated with hydrogen chloride, again yielded the trihydrochloride melting at 80°. In order to detect, if possible, any sesquiterpene alcohols in the tough, brown distillation residue, it was heated with phthalic acid anhydride to 100°. Upon treating the reaction product in the usual manner, it yielded a phthalic ester acid, which upon saponification with alcoholic potassium hydroxide, yielded an alcohol that was extremely difficultly volatile with water vapor. This alcohol, obtained in small amount, distilled *in vacuo* (2 mm.) between 135 and 137°. It is a very viscid, colorless oil with the peculiar odor of opopanax. With phenyl-*iso*cyanate it yielded a crystalline phenylurethane the melting point of which, however, could not be obtained constant in spite of several recrystallizations. Apparently it represents a mixture.

443. Mecca Balsam Oil.

Mecca balsam or balsam of Gilead *(Balsamum de Mecca vel gileadense seu judaicum vel Opobalsamum verum)* is the secretion obtained from the tips of shoots or from incisions of *Commiphora Opobalsamum* (L.), Engl. (family *Burseraceæ*) which occurs in southwestern Arabia and in Somaliland.

In Oriental medicine this balsam plays an important role. Possibly it never has entered European market in a pure condition, hence the results of the few investigations must be taken cautiously.

The volatile oil of the balsam was first prepared by J. B. Trommsdorff[2]) who found himself in possession of a presumably pure drug that had been shipped in conical lead

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[1]) Report of Schimmel & Co., October 1904, 67.
[2]) Trommsdorff's Neues Journ. der Pharm. 16, I. (1828), 62.

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flasks. Upon distillation with water vapor, 40 p. c. of an oil, with an odor reminding of lemon and rosemary, were obtained. A few years later Bonastre[1]) mentions a yield of only 10 p.c. A. Baur[2]) describes the oil, which likewise had been obtained by steam distillation, as a liquid with a turpentiny odor, the bulk of which distilled over between 153 and 157° (uncorr.).

444. Frankincense or Olibanum Oil.

Oleum Olibani. — Weihrauch- oder Olibanumöl. — Essence d'Oliban.

Origin and Production. In Somaliland and southeastern Arabia frankincense is obtained from *Boswellia Carterii*, Birdw. and other species of *Boswellia* (family *Burseraceæ*). Upon making incisions into the bark of the trees, a white emulsion exudes. After a time this congeals to yellow granules (tears or drops) which are either removed from the trunks or picked up from the ground.

Upon distillation with water vapor, frankincense yields from 5 to 9 p.c. of volatile oil.

Properties. Olibanum oil is colorless or yellowish and has an agreeably balsamic and faintly lemon-like odor. $d_{15°}$ 0.876 to 0.892. Whereas the former oils were lævogyrate, up to $-17°$ (comp. the first edition of this text-book), the oils distilled in the last ten years are dextrogyrate, α_D up to $+29°$. This would seem to indicate that the oleoresin is now collected principally from another species. $n_{D20°}$ 1.472 to 1.482; A. V. up to 3; E. V. 5 to 16; E. V. after acetylation 46.7 (one determination); soluble in 4 to 6 vol. of 90 p.c. alcohol, occasionally with slight turbidity.

Composition. The lævogyrate olibanum oil (See Properties) distills over mainly about 162°[3]). After repeated fractionation a lævogyrate hydrocarbon $C_{10}H_{16}$ boiling between 157 and 160° results. With hydrogen chloride it yields a monohydrochloride[4]) melting at 127°, with amyl nitrite and hydrochloric acid a nitroso-chloride melting at 100 to 101°. When boiled with alcoholic

[1]) Journ. de Pharm. 18 (1832), 333.
[2]) Arch. der Pharm. 233 (1895), 240.
[3]) J. Stenhouse, Liebig's Annalen 35 (1840), 306.
[4]) A. Kurbatow, *Ibidem* 173 (1874), 1.

potassium hydroxide the latter is converted quantitatively into
nitrosopinene $C_{10}H_{15}NO$ melting at 130˚. Hence it follows that
the terpene boiling between 157 and 160°, the olibene of Kur-
batow, is l-α-*pinene*[1]). Fraction 177 to 179˚, upon bromination,
yields dipentene tetrabromide[2]). Hence the second constituent
of the oil is *dipentene*. Inasmuch as olibanum oil yields the
phellandrene reaction with sodium nitrite and glacial acetic acid,
the third terpene contained in the oil is *phellandrene*[3]). In the
highest boiling portions the presence of *cadinene* has been
demonstrated.

The terpenes of the dextrogyrate oil (d_{15} 0.8775; α_D i 19 18′;
n_{D20} 1.47245; A. V. 1.8; E. V. 7.5) have been examined by
Schimmel & Co.[4]). From 6 kg. of oil 4.71 kg. of terpenes and
1.29 kg. of higher boiling products were obtained by fractionation.
Of the terpenes about 92 p.c. boiled between 156 and 161˚,
about 5 p.c. between 161 and 163° and about 4 p.c. between
163 and 181˚. In fraction 156 and 157˚ (d_{15} 0.862 to 0.863;
α_D + 30° 58′) the presence of i- and d-α-*pinene* was demonstrated
by the nitrosochloride and the nitrolpiperidide (m. p. 118˚), also
by its oxidation to pinonic acid (b. p. 170 to 175˚ under 7 mm.
pressure; m. p. of the active acid 69 to 70˚, of the inactive acid
104˚). In all fractions 158 to 164° the presence of *camphene*
was demonstrated by its conversion into borneol melting at 210
to 211˚. *Dipentene* was recognized by means of its tetrabromide
melting at 124˚, and p-*cymene* by oxidation of the last fraction,
by means of permanganate, to p-hydroxy*iso*propyl benzoic acid
melting at 156˚. β-Pinene, phellandrene and terpinene were not
present. 99 p.c. of the terpene fractions consisted of α-pinene
and camphene and but 1 p.c. of dipentene and cymene.

According to H. Hænsel[5]), olibanum oil contains an alcohol
$C_{26}H_{44}O$, named *olibanol*. It is a viscid oil which does not con-
geal in the cold and possesses an agreeable olibanum odor. B. p.
205 to 212˚ (17 mm.), 333 to 334˚ (751 mm.); d_{20} 0.9570 to 0.9596;
α_D — 65.05˚ to - 71.50˚.

[1]) Wallach, *Ibidem* 252 (1889), 100.
[2]) Observations made in the laboratory of Schimmel & Co.
[3]) Wallach. Liebig's Annalen 271 (1892), 297.
[4]) Report of Schimmel & Co. April 1914, 62.
[5]) Chem. Zentralbl. 1908, I. 1837; 1908, II. 1437.

The substance designated olibanol by E. Fromm and E. Autin[1]
is very different. It boils at 210 to 211° and has the formula $C_{10}H_{16}O$.

Olibanol has the properties of an alcohol, probably also those
of a ketone. This may be because it is a mixture of two sub-
stances, or because the substance has the capacity to react in
two tautomeric forms. Upon oxidation with potassium perman-
ganate in aqueous solution, olibanol yields a dibasic liquid acid
$C_{10}H_{16}O_4$. The constitution of this acid has not yet been ascer-
tained. In addition, olibanol loses one carbon atom and yields
pinononic acid, $C_9H_{14}O_3$. The proof that the substance in question
is really pinononic acid was demonstrated by treating it with
alkaline bromide-hypobromite solution when bromoform and nor-
pinic acid resulted. In addition, pinononic acid was characterized
by the preparation of its oxime (m. p. 187°) and its semicarbazone
(m. p. 209°). However, the structure of olibanol cannot be defi-
nitely inferred from the oxidation results.

From the oxidation liquid of the olibanol, d-*borneol* was iso-
lated (m. p. 201 to 202°), so that it may be assumed that olibanum
oil contains some borneol ester.

445. Mexican Linaloe (Lignaloe) Oil.

Oleum Linaloes. — Mexikanisches Linaloeöl. — Essence de Linaloé du Mexique.

Origin and Production. Mexican linaloe oil is obtained from
the wood and occasionally from the fruits of several species of
Bursera, more particularly from *B. Delpechiana* Poisson, presu-
mably it is also obtained from *B. Aloexylon* (Schiede), Engl. (*Ela-
phrium Aloexylon,* Schiede; *Amyris Linaloe,* La Llave); probably
also from *B. glabrifolia* (H. B. K.), Engl. (*B. penicillata* [Moç. et
Sessé], Engl.) and *B. fagaroides,* Engl. var. *ventricosa,* which is
reported to have a caraway-like odor[2]).

. The wood, known in Mexico as *Lignaloë* or *Linalué,* also as
Bois de citron du Mexique, occasionally is found in commerce
in trunk-like pieces of the thickness of a thigh. They are mostly
deprived of their bark, have an ash-gray exterior and are we-
thered. The cross section of the spongy, light wood reveals brown,

[1]) Liebig's Annalen 401 (1913), 253.
[2]) E. M. Holmes, Mexican Lignaloes. Perfum. Record 1 (1910), 57.

close concentric rings[1]). Wood distilled in Europe yielded 7 to 9 p.c. of oil.

As a rule the oil is distilled by the Mexican natives. According to information secured on the spot[2]), the oil is produced from two distinct but closely related species, *viz.* from the Spanish *Linaloe* and the *Copal limón*. The former has been almost completely exterminated, whereas the latter is still abundant. According to external characteristics and odor, the natives distinguish three varieties: fine, common, and caraway linaloe (possibly *B. lagaroides,* Engl. var. *ventricosa?*). The fine linaloe has a delicate and pleasant odor, the common is less agreeable, and the third has an odor reminding of caraway. The wood of the linaloe tree is said to be more compact than that of the *Copal limón* which is characterized as spongy. The commercial oil is distilled largely from the wood of the *Copal limón*. This tree (fig. 14) makes no great demand, growing on rocky soil. Although it can readily be propagated by means of cuttings, nobody seems to think of its propagation, though the young trees cannot be used for the production of oil until they are twenty years old. In recent years the oil that enters commerce is said frequently to have been obtained from fruits as well as wood. The fruits mature in September. The fleshy, greenish to red berries are of the size of Spanish peas *(garbanzo)*. They are sold in *Carga* quantities (one *carga* = 96 liters). The oil yield is 3 p.c. and is larger than that of the best wood. The distillation begins in July and continues into September. The fruits are removed by means of a crescent-shaped instrument so as to injure as little as possible of the flesh. The oil obtained by distillation possesses a herbaceous odor and resinifies very readily. For this reason it is not sold as such, but is added to the oil from the wood, which has better keeping qualities. In order to increase the quantity of the oil, also to improve it, the Indians subject the berries to a process of fermentation, previous to distillation, which causes the herbaceous odor to disappear. For this purpose they place the uninjured berries in boxes, cover them with bags, and thus subject

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[1]) The wood has been described by J. Collins, Pharmaceutical Journ. II. 10 (1869), 590.

[2]) Report of Schimmel & Co. October 1907, 59. — Comp. also Report of the Instituto Médico Nacional, Mexico 1904, January to March.

them to a uniform temperature for 3 to 4 days which causes them to mature (?) more fully.

The wood oil is best distilled from very old trees, 40 to 60 years old. In the case of young trees the attempt is made to increase the yield of oil by notching the stems. The increased yield of oil thus produced is to be regarded as as pathological product. The wounding is effected by removing strips of bark and wood 40 cm. long, 20 cm. wide and 5 cm. deep, either parallel to the axis of the stem or better diagonally thereto. If the removal of such a strip reveals that the tree has a "heart" *i. e.* a yellow colored, strongly aromatic wood, it can be used directly for distillation. If the tree has no "heart", it is allowed to stand with open wound so that it may acquire a "heart". For this purpose the wound is so inflicted that the rain water flowing down the trunk will not pass over the wound: the upper end is pointed and the lower margin made slanting so as not to accumulate foreign material that might cause decay. Should decay nevertheless set in, the injured parts are removed so as to prevent the spread of the decay and not to interfere with the production of the oil. If there is no interference, a change in the color of the wood may be observed after a few days. After a month a large part of the wood which was previously white and soft, has been changed to yellow and is much more strongly aromatic. The Indians were induced to adopt this practice by the observation that linaloe roots frequently contained so much oil that it could be expressed with the fingers, also that trees which had accidentally lost branches through wind storms, produced much oil and were very much changed in the course of years. This wounding, which converts trees poor in oil into trees rich in oil is done in April and September. The April wounding is not as effective as the wound inflicted in September. In either case the trees do not "mature" until January when the sap rises. During the months of October and November the trees lose their leaves.

The distillation is conducted principally from December to June in the most primitive manner. The wood of the trunk only is used. Many of the smaller distillers are wild Indians who do not speak Spanish. Real factories do not exist. The reason is presumably to be found in the difficult conditions of living in the linaloe districts. Vermin abounds and the Indians are inflicted

with contageous skin diseases (leprosy, &c.). The yield of oil
obtained in Mexico from the wood amounts at most to 2.5 p.c.

Fig. 14. Linaloe tree *(Copal limón)* in winter.

In Puebla the production amounts to about 4000 to 5000 kg.
annually. The oil is shipped in petroleum canisters of 16 to 17 kg.
capacity, two of which are crated together.

A representative of Schimmel & Co. had occasion to visit a distillery belonging to Lino Castillo, of Chiautla, Puebla. It is a larger village that may be reached from Puebla City in eleven hours. Whereas the elevation of Puebla is 2100 m. that of Chiautla is but 300 m. in a hilly country difficult of access and with little vegetation in spots.

With the exception of the copper helmet, all parts of the still are made of galvanized iron. The still, which is heated by direct fire, has a height of 1.5 m. and a diameter of 1.15 m. The lower part is provided with a piece of iron pipe which is closed with a wooden plug around which banana leaves are wrapped. Through it the water is drained off at the completion of the distillation. The helmet, which itself is provided with a condenser, is connected with a barrel condenser by means of two pipes. A pail or petroleum canister serves as receiver.

The stills are usually erected near a mountain stream and frequently remote from the trees that yield the material. The capacity of the apparatus is about 250 kg. of chips with which it is filled up to about 25 cm. from the upper margin. Enough water is added to cover the chips but so as to leave a margin of about 18 to 19 cm. when the cover is placed in position. The luting is effected with a black clay supported by wet rags.

A single still demands a force of six or seven Indians, four of whom comminute the wood. It is cut into thin slabs which are immediately transferred to bags in order to prevent evaporation of the volatile oil. One man can comminute between 70 and 100 kg. daily. A fifth man tends to the fire which is kept up exclusively with exhausted wood as fuel. The sixth man watches the distillation which requires from 18 to 20 hours per charge.

The price paid at the still for wood is 50 centavos (25 cents) for one arroba (= 11.5 kg.).

An oil distilled in Chiautla and secured on the spot, which probably had been obtained from *Bursera Alœxylon*, Engl. had the following properties: color, light yellow; d_{15} 0.8836; α_D — $10°58'$; $n_{D20°}$ 1.46377; A. V. 5.6; E. V. 19.3; soluble in 1.8 vol. or more of 70 p.c. alcohol.

Another oil distilled in Tepecuacuilco, Guerrero, under the eyes of the collector, had the following properties: d_{15} 0.8869; α_D — $10°6'$; A. V. 2.8; E. V. 18.3; soluble in 1.7 vol. or more of 70 p.c. alcohol [1]).

[1]) Report of Schimmel & Co. October 1907, 59.

The area in which Mexican linaloe oil is distilled, covers parts of the districts (states) of Oaxaca, Puebla, Guerrero,
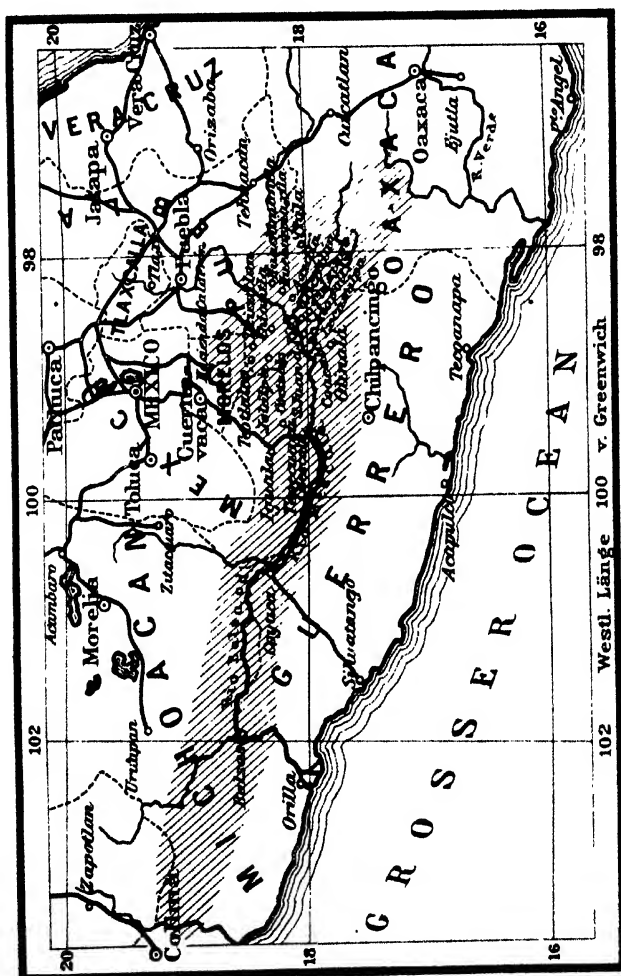
Fig. 15. Area of production of Mexican linaloe oil.

Morelos, Michoacan, and Colima. A special centre of production is found along the Rio Balsa, also known as Rio Mescala. The

localities in which the oil is distilled are: *Oaxaca*: Cuicatlan, Calihualac, Ingenio de la Pradera. *Puebla*: Chiautla, Chila, Coacalco, San Juan del Rio, Tzicatlan, Tulzingo, Teotlalco, Jolálpa, Coctzala, Ixcamilpa, Ocotlán, Huehuepiaxtla, Axutla, Huachimantla, Atopoltitlan. *Guerrero*: Olinalá (hence the original name of the oil "*olinaloe*"), Cualac, Iguala, Tepecuacuilco, Xalitla, Atzcala, Balsas, Cazalapan. *Morelos*: Hacienda Calderón.

Properties. The linaloe oil of commerce is a water-white or yellowish liquid of a pleasant odor[1]); d_{15} 0.875 to 0.891; α_D -3 to -14´; $n_{D20°}$ 1.460 to 1.465; A.V. up to 3.0; E.V. 1 to 42[2]); soluble in 1.5 to 2 vol. of 70 p.c. alcohol .and in 4 to 5 vol. or more of 60 p.c. alcohol.

Four oils distilled under supervision and taken directly from the receivers (comp. p. 122) had the following properties: d_{15} 0.8826 to 0.8869; α_D —10°6´ to —11°35´; $n_{D20°}$ 1.46179 to 1.46426; A.V. 1.8 to 5.6; E.V. 7.0 to 19.3; soluble in 1.7 to 1.9 vol. or more of 70 p.c. alcohol.

From the high optical rotation of these oils, the inference may be drawn that the lesser rotation of the commercial oils is due to admixture of the strongly dextrogyrate seed oils. That this practice prevails has already been pointed out under "Production".

Oils with somewhat different properties, notably as to specific gravity, were obtained by Schimmel & Co. from wood that was imported during the years 1895/96. d_{15} 0.8842 to 0.900; α_D —7°2´ to —19°24´; S.V. 8 to 9. The high specific gravity is accounted for by the large linalool oxide content which, judging from the odor, must be present in the oil.

According to Roure-Bertrand Fils[3]), the dextrogyrate oil that occasionally finds its way into commerce is the seed oil. With the exception of the optical rotation, which may be as high as ÷8°, the properties of this oil are the same as those of the wood oil.

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[1]) The odor, which is mostly described as lemon or rose-like, has not the least resemblance with the odor of either roses or lemons.

[2]) Occasionally ester values as high as 75 have been observed, though adulteration could not be detected.* Oils of this type had a decided odor of linalyl acetate. Report of Schimmel & Co. October 1912, 80.

[3]) Berichte von Roure-Bertrand Fils October 1907, 16; October 1908, 18.

Composition. Linaloe oil consists to the extent of 60 to 70 p.c. of an alcohol, $C_{10}H_{18}O$, which boils at 198 to 199° and which Morin[1]) first isolated from Cayenne oil and named licareol. Semmler[2]) then found it in the Mexican oil and upon closer examination ascertained that it was an aliphatic terpene alcohol and named it *linalool*. At first P. Barbier[3]) regarded linalool and licareol as different, but later he admitted their identity[4]). The linalool of the wood oil is lævogyrate, that of the seed oil is dextrogyrate.

According to Schimmel & Co., those portions of the wood oil that boil higher than linalool contain d-α-*terpineol* melting at 35° ($[\alpha]_{D_{20°}}$ + 29° 45'; m. p. of nitrosochloride 112°; m. p. of nitrolpiperidide 151 to 152°)[5]), also *geraniol* (m. p. of diphenylurethane 82°)[5])[6]).

An alcohol which previously had not been found in nature, *viz., methyl heptenol*, was likewise found in this oil by Schimmel & Co.[7]). It was isolated from one of the lower fractions boiling at 57 to 59° (2 to 3 mm.). Having been heated with phthalic acid anhydride for four hours on a water bath, the reaction product was treated in the usual manner. From the solution of the sodium salt of the acid phthalic ester steam distillation with alkali caused the isolation of an oil that reminded of octyl alcohol and methylheptenone. Its constants and the oxidation with chromic acid revealed it to be methylheptenol. The following properties were observed: d_{15} 0.8579; α_D — 1°34'; $n_{D_{20°}}$ 1.44951; b. p. 58 to 59° (3 mm.), 178 to 180° (under ordinary atmospheric pressure). The results of an elementary analysis were also in agreement with the formula $C_8H_{16}O$. Upon oxidation with chromic acid anhydride in glacial acetic acid solution, methylheptenol yielded a ketone, methyl heptenone, which also has been found to occur in linaloe oil[8]). (M. p. of semicarbazone 135 to 136°.)

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[1]) Compt. rend. 92 (1881), 998 and 94 (1882), 733. — Annal. de Chim. et Phys. V. 25 (1882), 427.

[2]) Berl. Berichte 24 (1891), 207.

[3]) Compt. rend. 114 (1892), 674 and 116 (1893), 883.

[4]) *Ibidem* 121 (1895), 168.

[5]) Report of Schimmel & Co. October 1900, 43.

[6]) *Ibidem* April 1892, 37.

[7]) *Ibidem* November 1908, 84.

[8]) *Ibidem* October 1894, 36.

According to Barbier[1]), linaloe oil is said to contain dimethyl-heptenol, a claim which, however, is merely based on the odor of a given fraction.

Linalool oxide, $C_{10}H_{18}O_2$, although it is contained only in traces in the oil, imparts to it a peculiar stuffy odor. A larger percentage of this substance is to be found in the oil distilled in Europe than in the oil distilled where the tree grows (comp. p. 124). Presumably its formation is due to oxidation of the linalool in the wood saturated with air.

Linalool monoxide was first prepared by N. Prileshaev[2]). Comparison of the synthetic product with the substance found in linaloe oil enabled Schimmel & Co.[3]) to establish the identity of the two. Both substances yield with phenyl*iso*cyanate a reaction product which solidifies only after having stood for months. The oily substances are removed by steam distillation and the residue is dissolved in petroleum ether, upon the evaporation of which the solid phenylurethane is left behind. Upon repeated recrystallization from dilute methyl or ethyl alcohol, prisms with a m. p. of 58.5 to 59° (synthetic) and 59 to 60° (natural) are obtained. The mixture of both phenylurethanes reveals no melting point depression.

According to P. Barbier and L. Bouveault[4]), linaloe oil also contains 3 p.c. of *sesquiterpenes,* further 0.1 p.c. of a monatomic and an equal amount of a diatomic terpene. Further data, however, are wanting.

That other hydrocarbons occur in the oil was shown by the investigations of Schimmel & Co.[5]).

While working on a larger amount of linaloe oil, a remarkably light, slightly optically active oil ($d_{15°} 0.7727$; $\alpha_{D\bullet} + 1° 46'$) was isolated which, under 18 mm. pressure, began to boil at 42° and, under ordinary pressure, distilled between 108 and 170°. After repeated fractionation under ordinary pressure over sodium, fractions were obtained that were optically inactive and the low density of which indicated petroleum hydrocarbons. Elementary

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[1]) Compt. rend. 126 (1898), 1423.
[2]) Berl. Berichte 42 (1909), 4811.
[3]) Report of Schimmel & Co. October 1912, 78.
[4]) Compt. rend. 121 (1895), 168.
[5]) Report of Schimmel & Co. April 1909, 69.

analysis revealed that fraction 120 to 145° consisted of *octylene* and *nonylene* and their isomers. A fraction having the boiling
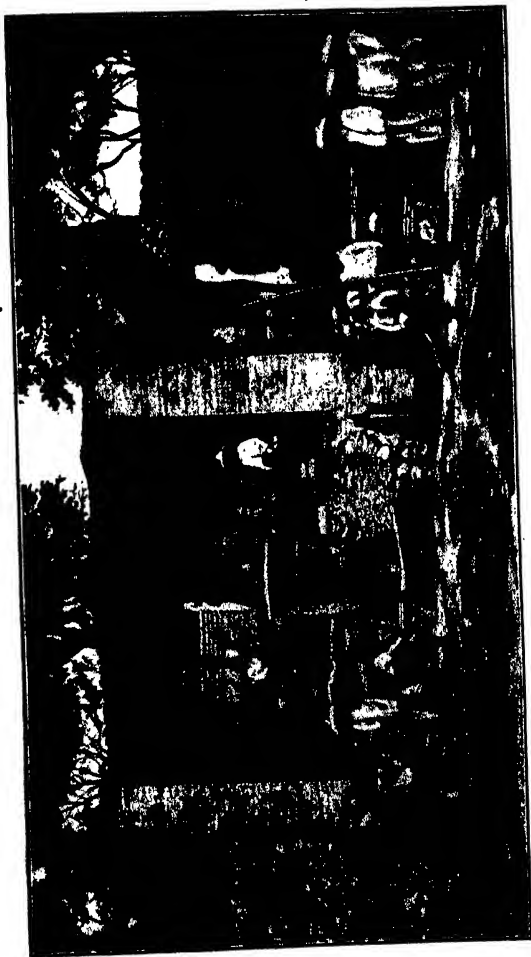
Fig. 16. Linaloe oil distillery in Chiautla (Mexico).

point of octylene had the following properties d_{15}, 0.7396; $a_D \pm 0°$; n_{D20}, 1.41255; b. p. 122 to 125°; and upon analysis yielded results in harmony with its composition.

Likewise, the physical constants and the results of the analysis of a nonylene fraction were in complete agreement with the composition and constants of this olefine: b. p. 139 to 142"; d_{15}. 0.7477; α_D : 0"; $n_{D20°}$ 1.41808.

Whether octylene and nonylene are normal constituents of the oil, or whether they represent added petroleum must remain undecided. That they should have been added to the oil as adulterant does not seem probable. For such purposes the amount was too small, being but 1 to 2 p. c. It may be that their presence can be explained by the use of petroleum canisters which had not been drained properly.

In addition it could be shown that the lower fractions of linaloe oil contained an *olefinic terpene*, $C_{10}H_{16}$, in addition to a terpene proper. This olefinic terpene is probably identical with myrcene. A fraction which was used for the identification of this terpene, after the removal of methylheptenone, had the following properties: b. p. 63 to 65° (16 mm.), 169 to 173° (under ordinary pressure); $d_{15°}$ 0.8243; $\alpha_D + 0°32'$; $n_{D20°}$ 1.46476. The results of an elementary analysis yielded results in agreement with the formula. When treated with glacial acetic acid-sulphuric acid, an alcohol with the properties of myrcenol, and upon reduction a hydrocarbon with constants in fair agreement with those of dihydromyrcene were obtained. However, crystalline derivatives could not be obtained either from the alcohol or the reduction product.

The terpene mentioned above, which accompanied the olefinic terpene, could not be identified either as bromide, as nitroso-chloride, or as nitrosite. Its presence, however, was indicated by the optical rotation, $\alpha_D + 8°41'$ of fraction 65 to 72° (16 mm.).

According to Schimmel & Co., the dextrogyrate oil mentioned on p. 124 contains d-*linalool* (m. p. of phenylurethane, 65°; α_D in 10 p. c. alcoholic solution $+ 1°6'$)[1], as principal constituent, also l-α-*terpineol* melting at 35° (m. p. of phenylurethane 112°)[2]; further *geraniol* (m. p. of diphenylurethane 82°)[2] and *nerol* (m. p. of diphenylurethane, 51 to 53°)[2]. The last-mentioned alcohol may also occur in the lævogyrate linaloe oil.

[1] Report of Schimmel & Co. October 1904, 56, footnote 1.
[2] *Ibidem* October 1905, 46.

Adulteration. The adulteration of linaloe oil with fatty oils, which has been observed here and there, is readily detected by the solubility test and by the greatly increased ester value. It should be noted, however, that occasionally oils with a high ester value (up to 75) have been observed[1]), an adulteration of which could not be proven. In such cases the high ester value had to be attributed to the presence of linalyl acetate. These oils naturally complied with the solubility requirements enumerated under Properties.

In one instance adulteration with terpineol[2]) was ascertained.

In doubtful cases repeated fractional distillation will render good service in passing judgement on the purity of an oil. From good oils as much as 62 to 72 p.c. of a linalool fraction can be obtained.

As substitute for linaloe oil, *shiu* oil (see vol. II, p. 508) has been recommended repeatedly in recent times. Inasmuch as adulteration with this oil suggests itself, it may be well to bear this in mind. In as much as shiu oil contains camphor, the detection of the presence of this ketone in a linaloe oil may be regarded as adulteration with shiu oil. For this purpose either of two methods may be employed[3]).

Detection of camphor by means of semicarbazide hydro-.chloride. To 25 gr. of oil distilled with water vapor a mixture of 1 g. semicarbazide hydrochloride, 1 g. sodium acetate and 25 cc. 90 p.c. alcohol is added. After standing 24 hours, 1 g. of sodium bicarbonate is added and the mixture distilled with steam. The distillation residue, contained in a dish, is evaporated somewhat on a water bath and then allowed to cool, when the camphor semicarbazone separates out. This may be admixed with some hydrazodicarbonamide, a decomposition product of the semicarbazide hydrochloride. · From the filtered precipitate the semicarbazone is dissolved with little alcohol, the hydrazodicarbonamide remaining behind. Upon evaporation of the alcohol the camphor semicarbazone is recovered. Hydrolyzed with dilute sulphuric acid it should reveal a decided odor of camphor. As a rule the melting point of the semicarbazone is not distinct because of admixed impurities which can be removed

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[1]) Report of Schimmel & Co. October 1912, 80.

[2]) *Ibidem* October 1909, 77.

[3]) *Ibidem* October 1913, 71.

only by repeated crystallizations. For this purpose the amount of substance is not apt to be sufficient.

With the aid of semicarbazide, the addition of 1 p.c. of camphor in linaloe oil can still be detected, more particularly if the reaction mixture is allowed to stand for more than 24 hours. A quantitative determination, however, is out of the question. Thus, a mixture of 80 p.c. linalool and 20 p.c. camphor yielded but 11 p.c. of the latter after two days. The other disadvantage of the method is that it requires so much time.

Much better results are obtained by determining the *camphor by means of oxidation with potassium permanganate*. In this manner the camphor content can be ascertained readily and with great accuracy.

For this purpose 50 g. of potassium permanganate and 300 cc. of water are transferred to a flask of 2 liter capacity and cooled by means of ice. With the aid of a graduated separating funnel 10 g. of linaloe oil are added drop by drop so as to require $\frac{1}{2}$ hour. The oil, which becomes very warm, is readily oxidized to a soluble product. After the reaction has been completed and the mixture no longer becomes warm (after about 2 hours), about 200 cc. of water are added and the unchanged camphor is distilled over with water vapor.

In this manner the addition of 1 p.c. of camphor or of 10 p.c. of shiu oil to linaloe oil could be detected. This test can be carried out in about 4 hours and is well adapted to the *quantitative* determination of camphor in linaloe oils adulterated with shiu oils. For the quantitative determination, salt should be added to the aqueous distillate and the latter shaken out repeatedly with ether. The ethereal solutions are combined and the residue weighed after the evaporation of the ether.

20 g. of mixtures of linalool and camphor being used the following results were obtained: —

From 80 p.c. linalool and 20 p.c. camphor 20 p.c.   camphor were recovered,
„   95 „   „   „   5 „   „   3 to 4 p.c.   „   „   „
„   99 „   „   „   1 „   „   0.75   „   „   „   „

This method being applied to a shiu oil ($d_{18°}$ 0.8790; α_D —11°10′; A.V. 0; E.V. 3.7; soluble in 3.8 vol. or more of 60 p.c. alcohol), a camphor content of 11.6 p.c. was ascertained. Linaloe oil, tested according to both methods, proved to be entirely free from camphor.

446. Carana Elemi Oil.

From Carana elemi from *Protium Carana* (Humb.), L. March. (family *Burseraceæ*) A. Tschirch and O. Saal[1]) obtained a volatile oil the odor of which reminded of fennel, dill and lemon and which distilled principally between 170 and 172°.

447. Conima Resin Oil.

The resin of *Icica heptaphylla*, Aubl. *(Protium heptaphyllum* [Aubl.], L. March., family *Burseraceæ)*, known as conima resin and as *Hyawa* gum is used as substitute for frankincense in British Guayana. It contains traces of a volatile oil[2]) which can be obtained by steam distillation.

The oil is yellowish and distills principally between 260 and 270°. The highest fractions have a bluish-green color. Distilled over sodium, a sesquiterpene, $C_{15}H_{24}$, *conimene*, boiling at 264 was isolated.

448. Manila Elemi Oil.

Oleum Elemi. — Manila-Elemiöl. — Essence d'Elemi.

Origin and Production. Manila elemi, known in commerce as elemi, is a soft, whitish turpentiny mass, which dries up in contact with air. It becomes waxy and acquires a yellow color. Until recently the botanical origin of this oleoresin, known as *Brea* in the Philippines, was not definitely known. E. D. Merrill[3]), however, has shown that the elemi tree, known as *Pili* by the natives, is *Canarium luzonicum* (Miq.), A. Gray (family *Burseraceæ*).

According to R. F. Bacon[4]) the resin flow is at its maximum when the tree produces new leaves. In Atimonan, district of Tayabas, the principal district of production, this takes place in January and June. During other parts of the year when the tree loses its foliage, it yields no resin. For the purpose of producing the balsam, the natives make incisions with their bolos. The oleoresin flows on the bark from which it is removed every few days before it has become dirty and hard. Healthy, fully

[1]) Arch. der Pharm. 241 (1903), 149.
[2]) J. Stenhouse and C. E. Groves, Liebig's Annalen 180 (1876), 253.
[3]) Gov. Lab. Pub. Manila 29 (1905), 51.
[4]) Philippine Journ. of Sc. 4 (1909), A, 93.

developed trees yield, on an average, as much as 4 to 5 kg. of balsam annually. A large tree yielded as much as 22 kg. of elemi in 2 months. In the fresh condition in which it exudes from the tree, this is always soft and becomes hard only when exposed to air and sunlight. Upon distillation with water vapor it yields 20 to 30 p.c. of oil.

Properties. Elemi oil of commerce is colorless or light yellow and possesses a decided odor of phellandrene. d_{15} 0.870 to 0.914; $\alpha_D + 35$ to $+ 53^\circ$); n_{D20} 1.479 to 1.489; A.V. up to 1.5; E.V. 4 to 8; soluble in 0.5 to 5 vol. of 90 p.c. alcohol, mostly soluble in 5 to 10 vol. of 80 p.c. alcohol. With sodium nitrite and glacial acetic acid the oil yields a decided phellandrene reaction.

Composition. According to Wallach[2]), the fraction·boiling below 175° contains d-α-*phellandrene*. In fraction 175 to 180° *dipentene* is abundant. It is specially suited for the preparation of dipentene derivatives. The dipentene was identified by means of its tetrabromide melting at 125°, its nitrosochloride and the conversion of the latter into the carvoxime melting at 93°.

The elemi oil of Deville[3]) likewise must have contained dipentene since it yielded a solid dihydrochloride.

In addition to these terpenes and polyterpenes, elemi oil also contains oxygenated substances which split off water when distilled, more particularly when heated with acid potassium sulphate[4]). As was shown by Schimmel & Co.[5]) they can be acetylated, hence are alcohols. From the acetylated oil a fraction was obtained which boiled at 82 to 83.5 (3 mm.), had an acetylation value of 196.5 and possessed a distinct odor of spearmint. However, it could not be proven that the substance in question was the acetate of dihydrocuminic alcohol[6]) previously found in gingergrass oil. Nevertheless, saponification of the ester fraction yielded an oil boiling between 220 and 230° the odor of which had great re-

[1]) An oil examined by Deville (Liebig's Annalen 71 [1849], 353) was strongly lævogyrate and probably obtained from a different kind of elemi. Comp. also J. Stenhouse, *ibidem* 35 (1840), 304.

[2]) Liebig's Annalen 246 (1888), 233; 252 (1889), 102.

[3]) *Loc. cit.*

[4]) Liebig's Annalen 246 (1888), 233; 252 (1889), 102.

[5]) Report of Schimmel & Co. April 1907, 41.

[6]) *Ibidem* April 1904, 56.

semblance with that of dihydrocuminic alcohol. Its characteristic naphthylurethane, however, could not be obtained.

A fraction 277 to 280° obtained by Schimmel & Co. was almost inactive and upon oxidation yielded an acid melting at about 170°. Later this fraction was investigated by Semmler[1]), who showed that in addition to a small amount of a *sesquiterpene alcohol*, the bulk consisted of a phenol ether, which he named *elemicin* and which proved to be allyltrimethoxy-3, 4, 5-benzene. An elemicin, freed from impurities as completely as possible by boiling with concentrated formic acid, had the following properties: b. p. 144 to 147° (10 mm.); d_{20}, 1.063; n_{D} 1.52848. Semmler oxidized elemicin in benzene solution with ozone. Upon destruction, with water, of the ozonides formed he obtained, in addition to trimethyl homo-gallic aldehyde, $C_{11}H_{14}O_4$ (b. p. 162 to 165° under 10 mm. pressure; m. p. of semicarbazone 188°), trimethyl homogallic acid, $C_{11}H_{14}O_5$, which melted at 119 to 120° and the formation of which is proof of the β, γ-position of the double linkage. When heated with sodium or with alcoholic potassium hydroxide, the allyl group is rearranged to the propenyl group with the formation of *isoelemicin* (b. p. 153 to 156° under 10 mm. pressure; d_{20} 1.073; n_{D} 1.54679; m. p. of dibromide 89 to 90°). Upon oxidation with permanganate, elemicin as well as *iso*elemicin yield trimethylgallic acid, $C_{10}H_{12}O_5$ (m. p. 169°; b. p. 225 to 227° under 10 mm. pressure; m. p. of methyl ester 84°; b. p. 166 to 167° under 10 mm. pressure). Oxidation of *iso*elemicin with ozone yields principally trimethylgallic aldehyde $C_{10}H_{12}O_4$ (m. p. 75°; b. p. 163 to 165° under 10 mm. pressure), the semicarbazone of which melts at 218°. When treated with acetic acid anhydride the oxime, which melts at 82 to 84°, could be converted into trimethylgallic acid nitrile melting at 93°.

The structural relationships of these compounds are expressed by the following formulas: —

| Elemicin | *Iso*elemicin | Trimethylgallic acid |
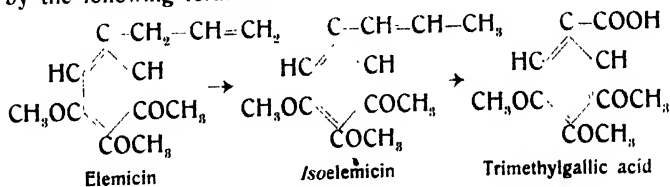
[1]) Berl. Berichte 41 (1908), 1768, 1918, 2183, 2556.

From 31 trees in the Philippines, designated by the botanist Merrill as *Canarium luzonicum*, A. M. Clover[1]) collected the oleoresin and distilled therefrom their oils. These revealed great differences but it was impossible to draw any generalisations relative to the age or sex of the tree. In the case of 10 oils, the terpene fractions consisted of pure d-*limonene*; 9 oils contained *phellandrene*; the terpene fraction of one oil was almost pure *terpinene* (m. p. of nitrite 155), that of another, almost pure *terpinolene* (m. p. of tetrabromide 116´).

The occurrence of terpinolene in nature had not been observed before, hence is noteworthy. Moreover, the terpinolene-containing oil was very remarkable. Even the crude oil distilled over within a range of one degree (the boiling point is not mentioned by Clover) and had a rotation of + 4 . The reactions for terpinene and phellandrene gave negative results, but a bromide that melted at 116 to 117´ (turning brown and foaming) was obtained in the form of glistening scales (from alcohol). Hence the presence of terpinolene was inferred. According to Wallach terpinolene boils between 185 and 190 ; according to v. Baeyer the hydrocarbon, regenerated from its tetrabromide, boils between 183 and 185 . The terpinolene-containing oil was purified by treatment with potassium hydroxide, distilled *in vacuo* and then revealed the following properties: b. p. 173.5 to 175´ (ordinary pressure), 80 to 81 ' (under 37 mm. pressure); $d_{4'}^{80'}$ 0.8360; $\alpha_{D30°}$: 1.7´ ; n_{D30} 1.4701. It is noteworthy that the optical rotation had diminished appreciably between the second and third distillation although the oil had been distilled from the oleoresin only the previous day. In order to increase the change of the principal constituent of the oil, some of it was heated in a sealed tube in an oil bath of 200 ' for 3 hours. After that the distillate revealed an optical rotation of − 7.5 ' and yielded the phellandrene reaction though not strongly (m. p. of lævogyrate nitrite 119 to 120´). Five days later another attempt was made to prepare terpinolene tetrabromide. In its place, however, crystals of dipentene tetrabromide melting at 120 ' were obtained. After recrystallization they melted at 125 . In the meantime the optical rotation of the oil had changed

¹) Philippine Journ. of Sc. 2 (1907), A, 1. — Americ. chem. Journ. 39 (1908), 613.

from $+ 1.7°$ to $-1.6°$. After a lapse of five or six days more it had increased to $-9.8°$ and after a month to $-34.5°$, thus showing that the oil was undergoing a remarkable spontaneous change. Three months later the oil was distilled with steam. When dried the distillate showed $\alpha_{D30°} -- 38$, when the change had probably reached its maximum. The tetrabromide prepared with the aid of different solvents melted, after one recrystallization, at 120 to 123° without being colored brown. After further purification it melted at 125°. No doubt, because of the presence of much dipentene that of phellandrene could no longer be established by means of the nitrite reaction. Clover is of the opinion that the terpinolene, which appears to be very pure though a low boiling point was observed, upon standing for several weeks had changed to dipentene, some d-phellandrene and an unknown lævogyrate terpene.

These observations are of sufficient importance to demand substantiation in order that it may be ascertained how these real or supposed changes of the terpenes mentioned occur.

Similar observations on elemi terpenes have been made by R. F. Bacon[1]) who has collected samples of elemi from 62 trees (C. luzonicum) which had been carefully identified botanically. The material was collected in Calaog, in the district of Tayabas. Of the volatile oils only two contained d-limonene, all the others contained phellandrene. Of nine oils from oleoresins of another district, six contained limonene. Other elemi samples from Culion and the island of Mindanao yielded terpene fractions consisting exclusively of pinene. Bacon assumes three phellandrenes: one boiling between 165 and 169°, a second between 173 and 175° and a third between 175 and 178°.

Bacon also investigated the action of light and heat on limonene and phellandrene. In connection with the latter, the remarkable observation was made that, under the influence of sunlight, its optical rotation is greatly diminished, moreover, more decidedly than by heat. Limonene, on the other hand, is fairly stable toward light, i. e. its optical rotation is reduced but slightly.

[1]) Philippine Journ. of Sc. 4 (1909), A, 93.

449. Canarium Wood Oil.

Among the scent woods of India is one which, according to W. G. Boorsma[1]), is known as *Kajoe rasamala*[2]) in the drug market. It is derived from a species of *Canarium:* From New Guinea and the Moluccas it is imported via Macassar to Java. It burns with a storax-like odor and contains 0.2 p. c. of a volatile oil which possesses an aromatic odor and a burning taste. Petroleum ether extracted from the wood a small amount of fatty oil, ether extracted an ester-like substance (about 2 p. c.) and alcohol a product with the odor of storax (1.6 p. c.).

450. Oil of Canarium villosum.

Under the designation *pagsainguin* oil Schimmel & Co.[3]) obtained from the Philippine Bureau of Science in Manila an oil which was supposed to have been obtained from the oleoresin of *Canarium Cumingii*, Engl. According to R. F. Bacon[1]), however, this is incorrect, for the parent plant had since been identified as *Canarium villosum*, F. Vill.

The oil examined by Schimmel & Co.[3]) had the following properties: d_{15° 0.8627; $\alpha_D +11°3'$; n_{D20} 1.47245; soluble in 3 vol. or more of 90 p. c. alcohol. When distilled the oil passed over between 158 and 183°, the larger part (70 p. c.) distilling between 165 and 177°. The principal constituent appeared to be cymene.

Another oil is described by Bacon[4]). By distilling the resin in a vacuum of 4 to 6 mm. about 11 p. c. of oil were obtained having the odor of Manila elemi oil.

The presence of d-*α-pinene* (m. p. of hydrochloride 125°) and *dipentene* (m. p. of tetrabromide 124°) was demonstrated.

The aqueous distillate contained much *formic acid* although no decomposition was observed during the process of distillation.

p-Cymene, the presence of which was suspected by Schimmel & Co. in pagsainguin oil, could not be found. It may be assumed,

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[1]) Bull. du Dép. de l'Agricult. aux Indes Néerlandaises 1907, No. 7, p. 1; Report of Schimmel & Co. November 1908, 19.

[2]) Comp. also Rasamala Wood Oil, vol. II, p. 543.

[3]) Report of Schimmel & Co. October 1907, 40.

[4]) Philippine Journ. of Sc. 5 (1910), A, 257.

however, that the composition of the oleoresin of *C. villosum*, like that of *C. luzonicum*, is subject to change.

Somewhat later the examination of the above-mentioned oil was resumed by Schimmel & Co.[1]). The suspicion that *cymene* is present was verified. On the other hand, the remaining hydrocarbons found were not then observed by Bacon.

Of this oil only 45 g. were available. Under a pressure of 4 to 5 mm. it distilled between 34 and 50° and was resolved into the following fractions: 1) at 34° about 20 g. with a camphene-like odor; 2) between 34 and 43° about 5 g. which boiled between 167 and 171° under ordinary pressure; 3) between 43 and 50° about 15 g. which had the odor of cymene; 4) a residue of resinified oil.

Of the first fraction that portion which distilled between 161 and 164° under ordinary pressure, about 8 g. were hydrated with the aid of glacial acetic-sulphuric acid in the well known manner. The ester fraction (b. p. 65 to 80° under 5 mm.) of the reaction product was saponified with alcoholic potassium hydroxide. Although the resulting oil had a distinct odor of *iso*borneol, no solid alcohol could be isolated. Want of sufficient material prevented the definite establishment of the presence of *camphene*.

Of fractions 1 and 2, seven grams that boiled between 164 and 169° were tested for β-pinene by oxidation with alkaline permanganate solution cooled with ice. From the concentrated oxidation mixture, sodium nopinate crystallized out, which, upon the addition of acid, yielded nopinic acid. After repeated recrystallization from benzene it melted at 124 to 125°. This proves the presence of β-*pinene*.

Fraction 3 showed the following properties: d_{15} 0.8620; $\alpha_D + 8°26'$. The phellandrene test gave negative results. The bulk of this fraction boiled between 174.5 and 176°. Because of its unmistakable cymene odor it was first oxidized with dilute permanganate solution. The oil not affected in this way was recovered by steam distillation. Having practically the same properties as the original oil it was further oxidized with strong permanganate solution at water-bath temperature. In this manner

[1]) Report of Schimmel & Co. April 1914, 73.

a very small amount of p-hydroxy*iso*propyl benzoic acid melting at 155 was obtained; and from this, by heating with hydrochloric acid, p-*iso*propenyl benzoic acid melting at 159 to 160°. Thus the presence of p-*cymene* was demonstrated. In all probability, however, the fraction contained a terpene in addition to cymene. That portion of fraction 3 which boiled between 176 and 179 was tested for terpinene with the nitrosite test but gave negative results.

Hence the pagsainguin oil examined contained *β-pinene* as principal constituent, also p-*cymene* and probably *camphene*.

According to Bacon[1]), the Tacamahac elemi examined by A. Tschirch[2]) is probably identical with the oleoresin of *Canarium villosum*. Upon distillation with water vapor it yielded 2 p.c. of a volatile oil with a borneol-like odor, the bulk of which distilled over between 170 and 175 . The higher boiling fractions (up to 220°) were yellow and had an empyreumatic odor. Above 220° a brown oil with a disagreeably pungent odor distilled over[3]).

451. Uganda Elemi Oil.

African or Uganda elemi, from *Canarium Schweinfurthii,* Engl., is white or pale yellow in color and contains numerous dark spots and fragments of wood which impart a dirty appearance to the drug. A sample of the oleoresin contained 0.3 p.c. of ash; A.V. 29.4; S.V. 44.8 (both determined in connection with a selected, clean sample). Upon distillation with water vapor it yielded 11.2 p.c. of a pale straw-yellow oil ($d_{15°}$ 0.8451; $\alpha_D + 79°20'$) which contained much *phellandrene*[4]).

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[1]) Philippine Journ. of Sc. 4 (1909), A, 94.

[2]) *Die Harze und die Harzbehälter,* Leipzig 1906, p. 440. — A. Tschirch and O. Saal, Arch. der Pharm. 242 (1904), 362.

[3]) From the genuine tacamahac of commerce, the botanical origin of which is unknown, Tschirch and Saal (*loc. cit.,* 400) obtained about 3 p.c. of a yellowish volatile oil, the odor of which reminded only distantly of that of the typical elemi resins, and more of that of camphor and turpentine. The bulk of the oil distilled between 170 and 175° as a colorless liquid, whereas the balance came over between 175 and 210° with a dark color and a somewhat empyreumatic odor.

[4]) Bull. Imp. Inst. 6 (1908), 254.

452. Mauritius Elemi Oil.

The elemi of Mauritius is obtained from *Canarium pani-culatum* (Lam.), Benth. (*Colophonia mauritiana*, DC.; *Bursera paniculata*, Lam.).

Upon distillation with water vapor, this oleoresin yielded 3 p.c. of an oil with a peculiar odor reminding of dill, fennel and lemon. The bulk of the oil distilled between 170 and 175 [1]).

453. Rasamala Oil.

From the balsam of *Canarium microcarpum*, Willd., obtained in the Moluccas, 80.4 p.c. of oil were obtained by distillation in Buitenzorg [2]): $d_{27°}$ 0.930; α_D $+0°28'$; S.V. 2.8. The bulk of the oil boiled between 250 and 285° and appears to consist of sesqui-terpenes. A previously [3]) distilled oil had: d_{20} 0.924; α_D 51 24'.

454. Oil from liquid Lagam Balsam.

Under the designation *Minjak Lagam* two Lagam balsams are comprehended in the Dutch Indies. Of these one is liquid, whereas the other constitutes a more solid mass [1]).

According to L. van Itallie and M. Kerbosch [5]) the parent plant of the liquid Lagam balsam is *Canarium eupteron*, Miq. (family *Burseraceæ*). The balsam is an orange-yellow liquid with a faintly green fluorescence: d_{15} 0.912; A.V. 10.45; S.V. 14.8. Upon steam distillation 49 p.c. of a volatile oil with the following constants were obtained: d_{15} 0.9051; α_D $-7.5°$; n_{D24} 1.4972. Fully 93 p.c. distilled over between 258 and 261°. The rectified oil showed the following constants: b. p. 261 to 263°; d_{15} 0.905; α_D $-7.46°$; $n_{D16.5}$ 1.49935. These properties lead to the sup-position that the oil might contain *caryophyllene*. As a fact, it yielded both caryophyllene alcohol (m. p. 92 to 94°) and the blue nitrosite melting at 111 to 112°.

[1]) A. Tschirch, *Die Harze und die Harzbehälter*, Leipzig 1906, p. 437
[2]) *Jaarb. dep. Landb. in Ned.-Indiê*, Batavia 1912, 57.
[3]) *Ibidem* 1910, 50.
[4]) Concerning the solid Lagam balsam oil see p. 77.
[5]) Arch. der Pharm. 250 (1912), 199.

Previously G. Haussner[1]) had obtained 33 p. c. of an oil (d_{15} 0.923; α_{1}, --9.9°) from a Lagam balsam. Upon the action of hydrochloric acid, the oil yielded crystals that melted at 114° and the composition of which agreed with the formula $C_{20}H_{32}4HCl$.

W. R. Tromp de Haas and J. Dekker[2]) have examined a Lagam balsam of the consistence of elemi (A.V. 26; S.V. 30) which yielded 21.5 p.c. of volatile oil concerning which, however, no further data are available.

In Buitenzorg[3]) two Lagam oils with the following properties have been studied: b. p. 245 to 255°; d_{24} 0.882 and 0.883; α_{0} --10° 12′ and --11°; A.V. 14.5 and 17; S.V. 15.7 and 20. The yield was 10.9 and 14.8 p.c. respectively.

455. Cameroon Elemi Oil.

From an African or Cameroon Elemi[4]), 15 to 20 p.c. of a colorless, mobile oil were obtained with d 0.953. It boiled, in the main, between 160 and 175°. Fraction 175 to 200° was colored brown[5]).

456. Nigeria Elemi Oil.

An elemi from South Nigeria has been examined in the Imperial Institute[6]) of London. Its botanical origin is not known. The oleoresin was whitish to light yellow or greenish in color, rather firm in consistence and permeated with brown spots and vegetable fragments. A.V. 55.3; S.V. 71.9. The yield of volatile oil was 8.1 p.c. This was of a pale straw color and contained

[1]) Arch. der Pharm. 221 (1883), 245.

[2]) Jaarb. dep. Landb. in Ned.-Indië, Batavia 1909, 66, 81.

[3]) Ibidem 1911, 48.

[4]) In a paper read before the 85. Versammlung deutscher Naturforscher und Ärzte K. Dieterich (Pharm. Ztg. 58 [1913], 774) reports on a West African (Cameroon) elemi resin, the botanical origin of which is completely in the dark. Presumably the Cameroon elemis are products collected from various Burseraceæ, among them Canarium Schweinfurthii (see Uganda elemi oil p. 138). In Ossidinge Dr. Mansfeld discovered a new Canarium species which has been named after him C. Mansfeldianum and which likewise yields elemi.

[5]) A. Tschirch and J. Cremer, Arch. der Pharm. 240 (1902), 320.

[6]) Bull. Imp. Inst. 6 (1908), 252.

much *phellandrene*. The constants given for the oil are: d_{15} 0.8686; $[\alpha]_D + 50° 30'$.

A second sample (A. V. 37.8; S. V. 46.2) contained 4.4 p. c. of volatile oil.

457. Oil of Dacryodes hexandra.

West Indian elemi oil is derived from *Tabonuco,* an oleoresin obtained copiously from *Dacryodes hexandra,* Griseb. (*Pachylobus hexandrus,* Griseb.), a species of the *Burseraceæ* native to Dominica, Martinique and Porto Rico. The oleoresin is collected from the living trees and is used in the production of torches and the manufacture of lacquer. The crude oleoresin is a very tough, white, strongly aromatic mass. According to A. More[1]) it yields, upon steam distillation, about 16 p.c. of a readily volatile oil. Schimmel & Co.[2]) obtained slightly more than 16 p.c. d_{15} 0.8875; α_D 13 20'. Upon fractional distillation the oil passed over between 156 and 180° leaving a residue of about 12 to 13 p.c.[1]) In the lowest fraction the presence of l-α-*pinene* was established (m. p. of hydrochloride 128°). When saturated with hydrogen chloride, fraction 173 to 176', which likewise was lævogyrate, yielded a crystalline hydrochloride that melted at 71° thus indicating the presence of l-*sylvestrene*.

Inasmuch as *l*-sylvestrene had not previously been found in a volatile oil, verification of this result was desirable. For this purpose Schimmel & Co.[3]) resumed the examination of their oil mentioned above and distilled in 1901. Its properties now were: d_{15}' 0.8880; α_D -- 13° 40'; A. V. 1.2; E. V. 11.2, E. V. after acetylation 56.0. Into the corresponding fractions of the oil hydrogen chloride was carefully passed. From fraction 168 to 171° the purest hydrochloride melting at 68° was obtained, whereas the hydrochloride from fraction 171 to 178° melted in large part at 63°, colored yellow when exposed to the light and was slightly decomposed. In addition large amounts of hydrochloride resulted which remained liquid in the freezing mixture.

For the further characterization of the *l*-sylvestrene, 20 g. of the hydrochloride from fraction 173 to 175° melting at 68° and with

[1]) Journ. chem. Soc. 75 (1899), 718.
[2]) Report of Schimmel & Co. October 1901, 20.
[3]) *Ibidem* April 1914, 50.

$[\alpha]_D$ — 19.5 , were heated with 20 g. aniline and 5 cc. of alcohol over a wire gauze until. aniline hydrochloride separated. Glacial acetic acid was then added and the mixture distilled with steam. The l-sylvestrene thus regenerated (about 10 g.) revealed the following properties: b. p. 172 to 180°; $d_{15°}$ 0.8604; α_D — 45 '0'; n_{D20} 1.47838. With acetic acid anhydride and sulphuric acid it yielded the intense blue color reaction for sylvestrene.

In order to prove positively that the terpene contained in *Dacryodes hexandra* is l-sylvestrene, Schimmel & Co. mixed the l-hydrochloride melting at 68 with an equal amount of d-hydrochloride melting at 71° and recrystallized the mixture from methyl alcohol. Thus inactive carvestrene hydrochloride melting sharply at 52° was obtained. Hence More's observation that l-sylvestrene is present was verified.

In the lowest fraction (b. p. 156 to 160°) the presence of *α-pinene* (m. p. of nitrolbenzylamide 122°) was demonstrated. Fraction 164 to 167 was tested repeatedly for *β-*pinene but without success. Traces of *camphene* appear to be present in fraction 164 to 167 for upon hydration and subsequent saponification a small amount of oil was obtained which, after treatment with potassium permanganate, had the odor of camphor.

Family: MELIACEÆ.

458. Cedrela Wood Oil.

Approximately twelve species of *Cedrela* (family *Meliaceæ*) that are native to America yield woods, with an agreeable odor, that are used in the manufacture of cigar and ·sugar boxes. These woods are erroneously designated cedar wood.

From a number of these woods volatile oils have been distilled, but only in a single instance has the botanical source been determined with certainty.

1.) *Cedrela oil.* From the wood of *Cedrela odorata*, L. (*C. cedro*, Loefl.; *Cedrus odorata*, Mill.) F. Rabak[1]) obtained 0.3 p.c. of a golden-yellow oil with an odor reminding of cedar. It had the following properties:' $d_{25°}$ 0.947; n_{D25} 1.5038; A.V. 3.9;

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[1]) Midland Drugg. and pharm. Review 45 (1911), 486.

E. V. 41.5; E. V. after acetylation 51; it formed a turbid solution with 80 p.c. alcohol.

2.) *Cedrela wood from Corinto*, Nicaragua[1]): yield 2.3 p.c.; a yellow oil with a specific gravity of 0.906 and an angle of rotation α_D — 17° 23'.

3.) *Cedrela wood from Cuba*[1]): yield 1.75 p.c.; a slightly yellow colored oil with a specific gravity of 0.923 and an angle of rotation α_D + 18 6'. It contains a considerable amount of *cadinene*, the lævogyrate hydrochloride of which, melting at 118 , was prepared.

4.) *Cedrela wood from La Plata*[1]): yield 0.59 p.c.; an optically inactive oil of a light blue color and a specific gravity of 0.928.

5.) *Cedrela wood from Punta Arenas*, Costa Rica[1]): yield 3.06 p.c.; a light blue oil boiling between 265 and 270°: specific gravity 0.915; α_D — 5° 53'. It consists largely of *cadinene* as was demonstrated by the preparation of the dihydrochloride melting at 118°.

6.) *Cedrela wood from Cedrela brasiliensis (Cedrela odorata*, L.?) *from Porto Alegre*[2]). From the saw dust of this wood only 0.5 p.c. of a light blue oil with a specific gravity of 0.9348 and an angle of rotation α_D - 0' 22' were obtained. The oil is possibly identical with that obtained from the La Plata cedrela wood.

459. Oil from Cedrela Velloziana.

Cedrela Velloziana, Roem., a tree 30 to 45 m. high, is known in Brazil as red or fragrant cedar.

The fresh capsules which have an odor of garlic, yield 0.007 p.c. of a yellow, limpid volatile oil upon distillation. It has a penetrating, unpleasant odor reminding somewhat of asafetida. It was lighter than water. Applied to the skin it acted as rubifacient but did not produce blisters.

The air-dried bark yielded 0.019 p.c. of volatile oil. It was limpid, of yellow color, lighter than water, and had a penetrating turpentine-like odor and burning, spicy taste[3]).

[1]) Report of Schimmel & Co. April 1892, 54.
[2]) *Ibidem* April 1896, 63. According to the Index Kewensis *Cedrela fissilis*, Vell. is synonymous with *C. brasiliensis*, Juss.
[3]) Th. Peckolt, Berichte d. deutsch. pharm. Ges. 11 (1901), 356.

Family: POLYGALACEÆ.

460. Senega Root Oil.

According to L. Reuter[1]), the root of *Polygala Senega*, L. (family *Polygalaceæ*), indigenous to eastern North America, contains 0.25 to 0.33 p.c. of a volatile oil which consists of a mixture of *methyl salicylate* and an *ester of valeric acid.*

A number of other species of *Polygala* likewise yield methyl salicylate upon distillation. P. van Romburgh[2]) found this ester in the roots of *Polygala variabilis*, H. B. et K. *β. albiflora*, D.C. that of *Polygala oleifera*, Heckel and that of *Polygala javana*.

Bourquelot[3]) proved the presence of methyl salicylate in the roots of *Polygala vulgaris*, L., *Polygala calcarea*, F. Schultz and *Polygala depressa*, Wenderoth.

From the investigations of Bourquelot it becomes apparent that the methyl salicylate is not present in the root as such but results from the action of the enzyme *gaultherase*[4]) on the glucoside *gaultherin*.

Family: EUPHORBIACEÆ.

461. Cascarilla Oil.

Oleum Cascarillæ. — Cascarillöl. — Essence de Cascarille.

Origin. Cascarilla bark from the Bahama islands and used principally in pharmacy is obtained from *Croton Eluteria*, Bennett and *C. Cascarilla*, Bennett (family *Euphorbiaceæ*). Upon distillation it yields 1.5 to 3 p.c. of volatile oil.

Properties. Cascarilla oil is yellow to greenish in color and has a faintly aromatic odor and taste. $d_{15°}$ 0.900 to 0.925;

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[1]) Arch. der Pharm. 227 (1889), 313.

[2]) Recueil des trav. chim. des P.-B. 13 (1894), 421; Chem. Zentralbl. 1895, I. 848.

[3]) Compt. rend. 119 (1894), 802, — Journ. de Pharm. et Chim. V. 30 (1894), 96, 188, 433; VI. 3 (1896), 577.

[4]) Named *betulase* by A. Schneegans (Journal der Pharmacie von Elsaß-Lothringen 28 [1896], 17).

$\alpha_D + 1$ to $+ 13^\circ$; n_{D20° 1.491 to 1.496; A.V. 3 to 9; E.V. 5 to 12; E.V. after acetylation (5 determinations) 67 to 72; readily soluble in 90 p.c. alcohol.

Composition. The older investigations revealed no constituent of the oil. K. Voelckel[1]) separated the oil by steam distillation into two portions. The first fraction was limpid, boiled at 173°, had the specific gravity of 0.862 and was almost free of oxygen. The second fraction was viscid and contained oxygen. According to Gladstone[2]) the oil consists of two hydrocarbons, one of which has a lemon-like odor, boils at 172° and presumably is *dipentene*[3]). The second hydrocarbon is said to resemble calamus oil and presumably is a sesquiterpene.

The more recent investigation of G. Fendler[4]) affords a better insight into the composition of the oil. The acid reaction of the cascarilla oil examined by him (d_{15° 0.914; $[\alpha]_{D15^\circ} + 4.81^\circ$) was due to an acid content of 2 p.c. which was removed by shaking the ethereal solution of the oil with dilute soda solution. By means of fractional distillation the acid mixture was resolved into a liquid distillate and a crystalline residue. The former consisted of an acid $C_{11}H_{20}O_2$, isomeric with undecylenic acid and named *cascarillic acid*. It boiled at 270°, had a specific gravity of 0.9324 at 20° and melted at — 18 . The melting point of the amide $C_{10}H_{19}CONH_2$ was observed at 78´. The crystalline residue, after recrystallization from dilute alcohol, melted at 58´. Judging from the analysis of the silver salt is consisted of a mixture of 80 p.c. *palmitic* and 20 p.c. *stearic acid*.

The free acids having been removed, the oil was shaken with 1 p.c. potassium hydroxide solution. In this manner 0.3 p.c. of *eugenol* (m.p. of benzoyl compound 71°; analysis) was isolated.

The lowest fraction of cascarilla oil distilled over between 155 to 157°; specific gravity 0.845 at 20°; $\alpha_D + 2.11^\circ$ at 21°. The addition of one molecule of hydrogen chloride and of two

[1]) Liebig's Annalen 35 (1840), 307; comp. also Trommsdorff, Trommsdorff's Neues Journ. d. Pharm. 26, II. (1833), 136.

[2]) Journ. chem. Soc. 17 (1864), 1; Jahresber. d. Chem. 1863, 547.

[3]) J. W. Brühl, Berl. Berichte 21 (1888), 152.

[4]) Arch. der Pharm. 288 (1900), 671. — H. Thoms, Apotheker Ztg. 14 (1899), 562.

molecules of bromine yielded oily products. The nitrosochloride melted at 91 to 92°, the nitrolpiperidide at 112°. Hence the terpene cannot be regarded as identical with pinene.

In fraction 170 to 173° the presence of *cymene* was proven by the formation of cymene sulphonate of barium and of *p*-hydroxy-*iso*propyl benzoic acid melting at 155 to 156°. Presumably traces of l-*limonene* are also contained in this fraction.

The higher fractions of cascarilla oil consist of two sesquiterpenes boiling between 255 and 257° and 260 and 265° respectively, also of an alcohol $C_{15}H_{28}OH$ boiling between 280 and 290°. None of these three compounds yielded characteristic derivatives.

462. Oil of Croton gratissimus.

The shrub *Croton gratissimus*, Burch. *(Euphorbiaceæ)*, a native of South Africa is used as a perfume on account of its fragrance[1].

It is widely distributed in German Southwest Africa and is used by the natives in the production of salves. Upon distillation a sample of fruits and leaves yielded 0.7 p.c. of a greenish oil the odor of which reminded of calamus oil[2].

463. Oil of Cathetus fasciculata.

Cathetus fasciculata, Lour. (*Phyllanthus cochinchinensis,* Muell.), a euphorbiaceous plant of China and Cochinchina, yields a volatile oil a sample of which was sent to Schimmel & Co.[3] from Annam, where the plant is known as *Bruyère*[4] *d'Annam*. The oil was of a greenish-blue color and its odor reminded of that of cajeput oil: d_{15}. 0.8897; α_D, — 4°34'; $n_{D20°}$ 1.47544; A. V. 1.9; E. V. 3.7; E. V. after acetylation 44.8 ≐ 12.7 p.c. of $C_{10}H_{18}O$; soluble in 0.5 vol. or more of 90 p.c. alcohol, of 80 p.c. alcohol 10 vol. were insufficient to effect solution. Of its con-

[1] D. A. Rosenthal, *Heil-, Nutz- und Giftpflanzen aller Länder.* Erlangen 1862, p. 835.

[2] Report of Schimmel & Co. October 1913, 111.

[3] *Ibidem* April 1914, 102.

[4] An Australian *"Essence de bruyère"*, the botanical origin of which is unknown, was described in the Report of Schimmel & Co. April 1904, 97. The aromatic oil had a pleasant odor and was of a light greenish-blue color (traces of copper): d_{15}. 0.8587, α_D ɟ 2°44', soluble in 4.5 vol. and more of 90 p.c. alcohol.

stituents, *cineol* should be mentioned which was identified by means of its iodol compound melting at 112°. Judging by the odor, cymene and linalool are present.

Similar in its properties was a sample of *Essence de bruyère du Tonkin* sent to the firm a number of years previously. However, the angle of rotation was different: $d_{15°}$ 0.8787; α_D + 10°32'; n_{D20} 1.47009; A. V. 1.7; E. V. 5.9; E. V. after acetylation 45.2; soluble in 0.3 vol. or more of 90 p.c. alcohol. In this sample also the presence of cineol was demonstrated by means of the iodol reaction. It may be assumed therefore that *Cathetus fasciculata* is the plant from which this oil was likewise obtained.

464. Oil of Excœcaria Agallocha.

Among the fragrant woods used in the tropics, the excœcaria wood from *Excœcaria Agallocha*, L. (family *Euphorbiaceæ*) plays a role of some importance[1]. In some parts of Dutch East India it is used as fumigant under the name *Menengen*. However, only the heartwood of trees not too old burns with an aromatic smoke. When resinified, the wood is quite odorless, very hard, reddish-brown, in parts almost black, its section glossy. It has a bitter taste.

With water vapor but a small amount of volatile substances was obtained. Extracted with petroleum ether yielded 24 p.c. of a light yellow, varnish-like mass. It consisted of a mixture of two acids and an ester which have not yet been characterized. Further extraction of the wood with ether yielded 12 p.c. of an extract that contained an ester, the alcohol of which melts at 85°. Subsequent extraction with alcohol yielded 10 p.c. more of extract which was resolved into two parts by chloroform.

465. Stillingia Oil.

Stillingia sylvatica, L. (family *Euphorbiaceæ*) is indigenous to North America from Virginia to Florida and westward to Kansas and Texas. The root which is used as a cathartic yields 3.25 p.c. of oil upon distillation. This is light yellow in color and lighter than water[2].

[1] W. G. Boorsma, Bull. du dép. de l'agricult. aux Indes Néerlandaises 1907, Nr. 7, p. 1.
[2] W. Bichy, Americ. Journ. Pharm. 57 (1885), 531.

466. Oil of Euphorbia pilulifera.

According to F. B. Power and H. Browning[1]), *Euphorbia pilulifera*, L., a euphorbiaceous plant of the Fiji islands, yields 0.018 p. c. of a volatile oil that boils between 235 and 260° and yields the color reaction for *furfurol*.

Family: ANACARDIACEÆ.

467. Mastic Oil.

Oleum Masticis. — Mastixöl. - Essence de Mastiche.

Origin. Mastic consists of the air-dried resinous sap of *Pistacia Lentiscus*, L., an evergreen plant of the family *Anacardiaceæ*. It grows in several islands of the Mediterranean and along the southern coast of this sea as far as Morocco and the Canary islands. The principal production centre of the resin is the island of Chios in which the· tree is cultivated for this purpose. From the slight incisions made in the trunk and heavier branches, the resinous juice exudes which dries to spherical, colorless grains.

Upon distillation mastic yields 1 to 3 p. c. of volatile oil.

Properties. Mastic oil is colorless and has the strong balsamic odor of the drug from which it is distilled[2]). d_{15° 0.857 to 0.903; $\alpha_D + 22$ to 34·; n_{D20° 1.468 to 1.476; A.V. up to 5; E. V. 2.5 to 19; E. V. after acetylation 17 to 21 (3 determinations). It is rather difficultly soluble in alcohol: of 90 p. c. alcohol 4 to 10 vol. are required and of 95 p. c. alcohol 0.2 to 2 vol. Mostly, however, the solutions are not perfectly clear and the further addition of solvent produces opalescence and even turbidity.

Composition. The oil begins to boil at 155°[3]) and passes over in large part at 160°. With dilute acids it forms terpin hydrate. Hence the principal constituent of mastic oil appears to be d-*pinene*. In order to provide a more direct proof of the identity of this hydrocarbon, the first fraction of the oil obtained

[1]) Pharmaceutical Journ. **90** (1913), 506.

[2]) Report of Schimmel & Co. April **1898**, 72.

[3]) F. A. Flückiger, Arch. der Pharm. **219** (1881), 170.

by steam distillation was collected separately and examined[1]).
It had the following properties: b.p. 156 to about 170°; $d_{15°}$ 0.8599;
$a_D + 32°57'$; $n_{D20°}$ 1.46925. A phellandrene test gave negative
results. Fraction 156 to 157° (d_{15} 0.8615; $a_D + 39°14'$) yielded
but a nominal amount of nitrosochloride melting at 106° (m.p.
of benzylamine base 123 to 124°). The small yield of nitroso-
chloride in so active a pinene fraction renders possible the
presence of active and inactive a-pinene. In order to determine
the presence of both an attempt was made to obtain the corres-
ponding pinonic acids. Yet, it was possible only to prove the
presence of d-a-*pinene* by oxidation to d-pinonic acid melting at ·
104° ([a]$_D$ +90.15° [8.8717 p.c. chloroform solution]; m.p. of
semicarbazone 204°). However, other hydrocarbons appear to
be present, for in addition to the pinonic acid, acids melting
at 95 to 98° and 183 to 185° respectively were formed, but could
not be identified. Fraction 159 to 162°, in which β-pinene or
sabinene were suspected did not, upon oxidation with perman-
ganate, yield the characteristic oxidation products for these
hydrocarbons, but oxalic acid.

Hence mastic oil contains principally d-a-pinene and little
inactive a-pinene. In addition a second terpene, not characterized
thus far, appears to be present.

An oil[2]) distilled from the *leaves* of the mastic tree had the
properties: d 0.887; $a_D + 3°$. It contained 5.8 p.c. of ester and
13.5 p.c. of acetylizable constituents, also pinene and presum-
ably other terpenes and sesquiterpenes. Its odor reminds of that
of the oils of rue and savin.

468. Chios Turpentine Oil.

Origin. Chios turpentine, known to the ancients[3]), is obtained
by making incisions into the trunk of *Pistacia Terebinthus*, L.
(family *Anacardiaceæ*), a tree found in the Orient. It is produced

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[1]) Observations made in the laboratory of Schimmel & Co.

[2]) Perfum. Record 4 (1913), 403.

[3]) Chios Turpentine is the τέρμινθη. of Theophrastus and the τιρίμινθος
of other authors. It is from this word that the present designation of tur-
pentine for the resinous exudations of various species of *Pinus* is derived,
F. A. Flückiger and D. Hanbury, Pharmacographia, London 1879, p. 166.

principally in the island of Chios. Chios turpentine has the consistence of ordinary coniferous turpentine and, like it, consists of a mixture of resin and volatile oil. Upon distillation it yields 14 p. c. of oil.

Properties. Chios turpentine oil has an agreeable, mildly turpentine-like odor which at the same time reminds somewhat of mace and camphor. $d_{15°}$ 0.868 to 0.869; $\alpha_D + 12°6'$[1]) to $19°45'$[2]).

Composition. After treatment with sodium the oil boiled at 157° and elementary analysis revealed that it had the composition $C_{10}H_{16}$. With dry hydrogen chloride the distillate yielded a solid compound[3]) after several weeks. It thus becomes apparent that, like the ordinary turpentine oil, Chios turpentine oil consists largely of *α-pinene.*

From the resinous sap of *Pistacia Terebinthus* var. *palæstina*, Engl. L. Reutter[4]) obtained 11 p. c. of volatile oil from which small crystals of *borneol* (details as to identification wanting) separated. The oil had a specific gravity of 0.8516; $\alpha_D - 17°18'$; n 1.4622.

469. Schinus Oils.

Origin. The Peruvian pepper tree, *Schinus molle*, L. (Ger. *Mollebaum;* family *Anacardiaceæ*), a native of South America is frequently cultivated in southern Europe on account of its handsome pennate leaves and fragrant flower clusters. The aromatic berries are used in the preparation of a vinous beverage. Their taste at first is sweet, then spicy and finally peppery, hence in Greece they are frequently used as a substitute for pepper. The odor of the fruit, like that of the leaves, resembles elemi, but also that of pepper and juniper.

OIL OF THE FRUITS.

Yield. Upon distillation, the fruits yield 3.35[5]) to 5.2[6]) p. c. of volatile oil.

[1]) Flückiger, Arch. der Pharm. 219 (1881), 170.
[2]) Report of Schimmel & Co. October 1895, 63.
[3]) Flückiger, Arch. der Pharm. 219 (1881), 170.
[4]) Schweiz. Wochenschr. f. Chem. u. Pharm. 51 (1913), 537.
[5]) H. Helbing, Jahresb. der Pharm. 1887, 25.
[6]) Report of Schimmel & Co. April 1897, 44.

Properties. It is a limpid oil with an odor of phellandrene. Schimmel & Co.[1]) observed the following constants: $d_{15°}$ 0.850; $\alpha_D + 46°4'$ at 17°; soluble in 3.3 parts or more of 90 p. c. alcohol. An oil distilled in Mexico had the following properties: $d_{15°}$ 0.8600; $\alpha_D + 42°30'$; E. V. 25.2; E. V. after acetylation 56.5; its solution in 98 p. c. alcohol is clear at first but upon the addition of 2 vol. or more a decided turbidity results.

Composition. Upon passing hydrogen chloride into the lowest fraction, G. Spica[2]) obtained a solid monohydrochloride melting at 115° the formation of which is probably due to α-*pinene*. From the fraction below 170° of an oil examined by E. Gildemeister and K. Stephan[3]) only minimal amounts of nitrosochloride could be obtained thus showing that but a small part of the oil, $1/2$ p.c. at most, consists of pinene. The bulk of the oil boiled between 170 and 174° (d 0.839; $\alpha_D + 60°21'$) and yielded a decided phellandrene reaction with sodium nitrite and acetic acid. As becomes apparent from the optical behavior of the several crystallizations of the nitrite, the phellandrene of the schinus oil consists of a mixture of much dextro-phellandrene with very little laevo-phellandrene. According to Wallach[1]), the hydrocarbon consists principally of d-α-*phellandrene*, but some *l-phellandrene* may also be present.

With the aid of alkali a phenol can be removed from the oil. Because of its nitrite, melting at 156°, Spica regarded it as thymol[3]). In the oil examined by Gildemeister and Stephan *carvacrol* (m. p. of *iso*cyanate 140') but no thymol was found.

In fraction 180 to 185°, which had been exposed to light for some time, Spica observed a crystalline substance that melted at 160° and which he suspected as being identical with the pinol hydrate, $C_{10}H_{16}O.H_2O$ discovered by Sobrero. Since pinol hydrate melts at 131° this possibility is excluded.

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[1]) Report of Schimmel & Co. April 1908, 121.

[2]) Gazz. chim. ital. 14 (1884), 204; Jahresber. d. Chem. 37 (1884), 1462.

[3]) Arch. der Pharm. 235 (1897), 589.

[4]) Nachr. K. Ges. Wiss. Göttingen 1905, Heft 1, 2; Chem. Zentralbl. 1905, II. 674.

[5]) Nitrosocarvacrol melts at 153°.

OIL OF THE LEAVES.

Properties. An oil obtained from Mexico[1]) had the following properties: d_{15}, 0.8583; α_{D} + 44°50'; $n_{D 20°}$ 1.47665; E. V. 7.2. An oil obtained from Algiers[2]) had the following properties: d_{15} 0.8658; α_{D} + 65°20'; E. V. 3.4; E. V. after acetylation 40.4. Two oils distilled in Algiers and Grasse respectively from twigs with leaves had the following properties[2]): d_{15}, 0.8634 and 0.8696; α_{D} + 50°54' and + 46°13'; E.V. 5.5 and 8.2; E.V. after acetylation 29.4 and 43.4.

Composition. Like the oil of the fruits that of the leaves contains large amounts of *phellandrene*[1]).

470. Oil of Rhus Cotinus.

From the young twigs of *Rhus Cotinus*, L. (*Cotinus coggygria*, Scop.; Ger. *Perückenbaum*; family *Anacardiaceæ*), G. Perrier and A. Fouchet[3]) obtained 0.1 p.c. of a colorless volatile oil that had a faint odor of turpentine and in other respects revealed the following properties: d_{15}, 0.875; α_{D} + 13"; n_{D} 1.4693; A. V: 6.1; S. V. 34.3. It was soluble in 17 p. of 80 p.c. alcohol, in 10 p. of 85 p.c. and in 3 p. of 90 p.c. alcohol. With 94 p.c. alcohol it was miscible in all proportions.

An oil distilled from leaves and flowers and sent to Schimmel & Co. from southern France as *Essence de Fustet* was examined by them. The odor of the faintly yellow almost colorless oil was that of the terpenes but also reminded somewhat of neroli. The following constants were observed: d_{15}, 0.8710; α_{D} + 32"54'; $n_{D 20°}$ 1.4887; A. V. 0.9; E. V. 20.4; soluble in 6 vol. or more of 90 p.c. alcohol.

Fractionation revealed that the oil consisted almost exclusively of terpenes. Upon testing the lowest boiling fraction of 161 to 164° (d_{15}, 0.8563) for *camphene* with glacial acetic acid and sulphuric acid, *isobornyl* acetate was obtained which, upon saponification, yielded *isoborneol*. In fraction 164 to 167° *β-pinene* could not be identified with certainty. Upon oxidation with alkaline

[1]) Report of Schimmel & Co. April 1908, 121.

[2]) Berichte von Roure-Bertrand Fils April 1909, 36. — G. Laloue, Bull. Soc. chim. IV. 7 (1910), 1107.

[3]) Bull. Soc. chim. IV. 5 (1909), 1074.

[4]) Report of Schimmel & Co. April 1913, 86.

permanganate, shiny scales of a difficultly soluble sodium salt were obtained which may possibly have been sodium nopinate. In fraction 170 to 174° phellandrene was not contained. Fraction 174 to 176° (d_{16} 0.8454; $\alpha_D + 54°40'$) contained *limonene* (m. p. of tetrabromide 103 to 104°; m. p. of dipentene dihydrochloride 50°).

471. Oil of Rhus aromatica.

Upon distillation the bark of *Rhus aromatica*, Ait. yields 0.07 p.c. of a dark brown oil with an acid reaction. In the cold solid particles separated and at —15° it completely solidified. d_{22} 0.954; A. V. 48.53; E. V. 16.8. It contains *palmitic acid* and *a phenol*[1]).

Family: AQUIFOLIACEÆ.

472. Paraguay Tea Oil.

From the dried leaves of *Ilex paraguayensis*, A. St. Hill. and other species of *Ilex* (family *Aquifoliaceæ*) known as Paraguay tea, H. Haensel[2]) obtained 0.775 p.c. of a dark yellow, solid oil that melted at 26.5°; d_{16} 0.8875; $[\alpha]_{D20} + 3.73°$; A.V. 61; S.V. 91.

Family: CELASTRACEÆ.

473. Oil of Euonymus atropurpureus.

From the root bark of *Euonymus atropurpureus*, Jacq., H. Rogerson[3]) obtained 0.01 p.c. of a volatile oil that boiled between 120 and 160° (25 mm.). It gave a decided reaction for *furfurol*. Upon standing a substance melting at 120° separated, possibly *furane-β-monocarboxylic acid*.

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[1]) H. Haensel, Apotheker Ztg. **26** (1911), 387.
[2]) Pharm. Ztg. **49** (1904), 335.
[3]) Journ. chem. Soc. **101** (1912), 1042.

Family: *SAPINDACEÆ*.

474. Oil of Serjania serrata.

Upon the distillation of the fresh leaves of *Serjania serrata*,
Radlkofer, a native of Brazil, Th. Peckolt[1]) obtained 0.1 p.c. of
a volatile oil, d_{15} 0.917. The penetrating odor was peculiar,
somewhat like civet.

The leaves of *Serjania piscatoria*, Radlkofer also yielded
0.03 p.c. of a limpid oil with an odor reminding of tobacco and
civet[2]).   •

Family: *VITACEÆ*.   •

475. Cognac Oil.

Oleum Vitis Viniferæ. — Cognacöl. - Huile Volatile de Cognac ou de Lie de Vin.

Origin and Production. The specific aroma of the wine (from
Vitis vinifera, L., family *Vitaceæ*) is produced by the ethereal
fusel oil of the wine. It is also known as cognac oil (Ger. *Drusen-
öl, Weinbeeröl, Weinhefenöl* and *Weinöl*) and is a product of
the ferment activity of the yeast. For this reason it is found
principally in the yeast which settles at the bottom after the
fermentation has been finished. The wine itself contains but
minimal amounts thereof, namely 1 in 40.000.

The formation of the bouquet of the wine has been investigated
by A. Rosenstiehl[3]). He found that the aroma of the wine is
due not only to the kind of grape but also to the organisms that
develop spontaneously on the fruit. As to the chemical changes
incident to its formation nothing definite is known. It is assumed
that a glucoside is involved in the formation of the aromatic
substance which is supposed to be the product of hydrolysis,
effected by an enzyme in the yeast.

For the production of the cognac oil either the liquid wine
yeast, that remains after the wine has been drawn off, or the

[1]) Bericht deutsch. pharm. Ges. 11 (1901), 366.
[2]) *Ibidem*, 362.
[3]) Compt. rend. 146 (1908), 1224, 1417; 147 (1908), 150. — Chem. Ztg. 32
(1908), 865; Chem. Zentralbl. 1908, II. 260, 534. 816, 1120.

press cakes, resulting from the expression of the liquid from the yeast, is employed. The distillation is conducted in rather primitive fashion in the wine-producing regions. Formerly a lead-lined barrel[1]) supplied with a condenser was used. The charge was heated with direct steam.

According to another description[2]) ordinary brandy stills are employed which are heated over direct fire. In order to prevent burning of the yeast they are provided with a stirring apparatus.

The yeast is mixed with water and, previous to the distillation, substances are added the purpose of which is not well understood. According to A. Rautert[1]), 250 g. of sulphuric acid are added to 50 kg. of dregs. This addition is said to make the mixture more limpid. In the Palatinate 2 p.c. of freshly slaked lime, 1 p.c. potassa and 1 p.c. common salt are added to the mixture of 1 part dregs and 5 parts water. The oil floats on the hydroalcoholic distillate in the receiver. From the latter more oil can be obtained by cohobation. The yield of cognac oil from the press cake is given as from 0.036 to 0.066 p.c. From Rhenish and Palatinate yeasts Schimmel & Co., however, obtained 0.07 to 0.12 p.c. of cognac oil.

Properties. Crude cognac oil, mostly colored green because of the presence of copper, contains large amounts of free fatty acids. Being odorless, these may be regarded as ballast of no value. For its purification the oil is therefore shaken first with a solution of tartaric acid to remove the copper, then with soda solution to remove the fatty acids. Thus purified it constitutes second grade cognac oil. The finest qualities are prepared from it by subsequent rectification. In this process the esters of the higher fatty acids with but a faint odor are not distilled over thereby strengthening the distillate. The physical properties of the three kinds of oil, the crude, the purified and the rectified, differ greatly. Because of insufficient observations, no general standards can be laid down.

Cognac oil possesses a benumbing odor which, in the undiluted condition, is disagreeable and nauseating. Frequently an

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[1]) Dingl. polytechn. Journ. 143 (1857), 71; Chem. Zentralbl. 1857, 57.
[2]) Chemist and Druggist 50 (1897), 183.

empyreumatic odor is also noticeable, due to carelessness in the distillation.

The specific gravities of various crude cognac oils obtained from the Mosel, Tirol, Rhenish Palatinate and the Rheingau varied between 0.872 and 0.890[1]); n_{D20} 1.427 to 1.432. Optically they were slightly lævogyrate and dextrogyrate, α_D — 0° 3′ to $+$ 0° 43′. In 70 p.c. alcohol the oil is but slightly soluble, of 80 p.c. alcohol $1^1/_2$ to 5 parts are required to yield a clear solution. The ester value fluctuates between 140 and 250, the acid value between 29 and 100 or more[2]).

Composition. Based on an investigation made by Pelouze[3]) and J. Liebig in 1836, ethyl œnanthate, $C_{18}H_{18}O_{3}$, was regarded as the principal constituent of cognac oil. Later Delffs[4]) claimed the œnanthic acid of the ester was identical with pelargonic acid. Then A. Fischer[5]) pointed out that the supposed chemical unit, *viz.* the œnanthic acid, was a mixture of much *caprinic acid* with little *caprylic acid*. In Hungarian cognac oil, F. Grimm[6]) likewise found caprinic and caprylic acids, the former predominating. From the non-acid part of the saponified oil Halenke and Kurtz[7]) obtained only *ethyl* and *amyl* alcohols but no butyl and propyl alcohols.

Hence the bulk of the cognac oil consists of the *amyl* and *ethyl* esters of *caprinic acid.* However, these two esters do not constitute the principal constituent since the specific odor of the oil is due to other substances that have not yet been determined.

Of interest is the analysis, by E. C. Morin[8]), of a genuine cognac distilled in 1883 in Surgères in the lower Charente. In 100 liters cognac he found the following substances in the amounts given: —

[1]) The cognac oil examined by Grimm (see later), judging it by its specific gravity 0.85 at 20°, must have contained alcohol.

[2]) Comp. also Report of Schimmel & Co. April 1899, 16.

[3]) Liebig's Annalen 19 (1836), 241.

[4]) Poggendorff's Annalen 84 (1851), 505. - Liebig's Annalen 80 (1851), 290.

[5]) Liebig's Annalen 118 (1861), 307.

[6]) *Ibidem* 157 (1871), 264.

[7]) *Ibidem*, 270.

[8]) Compt. rend. 105 (1887), 1019.

Aldehyde . . . . traces
Ethyl alcohol . . . . . . 50837.00 g.
Normal propyl alcohol . . . 27.17 g.
Isobutyl alcohol . . . . . 6.52 „
Amyl alcohol . . . . . . 190.21 „
Furfurol }
Bases } . . . . 2.19 „
Fragrant wine oil[1]) . . . . 7.61 „
Acetic acid . . . . traces
Butyric acid . . . . . . „
Isobutylene glycol . . . . 2.19 g.
Glycerin . . . . 4.38 „

C. Ordonneau[2]), on the other hand, obtained 218 g. of normal butyl alcohol from a hectoliter of a different cognac and regarded this as the characteristic product of the fermentation of the elliptical yeast. Later it was shown that the cognac examined by Ordonneau was probably distilled from a wine that contained the *Bacillus butyricus* and that the presence of the butyl alcohol, which is not found under ordinary conditions, was due to this organism.

From these investigations it becomes apparent that the cognac oil, when prepared as described above, by no means contains all of the substances found that occur in cognac. Hence it is impossible to prepare from the oil alone a product that is equal to distilled cognac.

Tests. The examination of cognac oil is generally restricted to a test for the possible presence of alcohol. For this purpose a definite amount of cognac oil is shaken in a graduated cylinder with an equal volume of water or glycerin. Alcohol, if present, would cause an increase in the water or glycerin layer.

According to Gehe & Co.[3]) the melting point of the isolated fatty acids admits of conclusions as to the purity of cognac oil. The mixture of the fatty acids of the genuine oil is said to be

[1]) Presumably identical with the cognac oil obtained from yeast.
[2]) Compt. rend. 102 (1886), 217; comp. also E. Claudon and E. C. Morin, *Ibidem* 104 (1887), 1109; further Sell, Arbeiten a. d. Kaiserl. Ges. Amt 6 (1890), 335.
[3]) Pharm. Zentralh. 43 (1902), 273.

liquid at ordinary temperature, whereas that of artificial cognac oil is solid, moreover the mixture of fatty acids from pure cognac oil, is scarcely rendered turbid at $+5^\circ$. Schimmel & Co. have not been able to verify these observations. Moreover, the fatty acids from genuine cognac oil also solidify upon standing.

Family: *GONYSTILACEÆ*.

476. Oil of Gonystilus Miquelianus.

The scent wood, known as *Kajoe garoe* in the Malay peninsula[1]), and derived from *Gonystilus Miquelianus*, Teysm. et Binn. (family *Gonystilaceæ*) yields, according to P. A. A. F. Eyken[2]), upon steam distillation a volatile oil that is solid at ordinary temperature and melts between 66 and 68°; b. p. 280 to 290 ; $[a]_D$ in absolute alcohol $+ 35°$. In order to remove resins, the oil, in ethereal solution, was washed with solution of potassium hydroxide, and, after evaporation of the ether distilled twice. Upon steam distillation, however, the colorless oil was decomposed yielding an acid distillate and solid resinous residue. The solid substance could be isolated by freezing it out. After recrystallization from acetic acid and alcohol it revealed the following characteristics: formula $C_{15}H_{26}O$; m. p. 82 ; b. p. 164 to 166° (17 mm.); mol. wt. computed 222, found 232 and 228; $[a]_D$; in absolute alcohol 30°. Eyken gave to it the name *gonystilol*. When boiled with formic acid, the alcohol was converted into a sesquiterpene gonystilene, $C_{15}H_{24}$; b. p. 137 to 139° (17 mm.); d_{17} 0.9183; $[a]_D$; in absolute alcohol $+ 40°$; mol. refr. found 66.7, computed for $C_{15}H_{24}O_{/2}$ 66.5. It is noteworthy that guajol and guajene have respectively the same degree of rotation but opposite in direction. Hydrogen chloride and bromine yielded only oily addition products. When treated according to Bertram and Walbaum with glacial acetic acid-sulphuric acid mixture no alcohol resulted. The sesquiterpene was recovered for the most part unchanged.

[1]) On aloe wood and other scented woods, by W. G. Boorsma. Bull. du dép. de l'agricult. aux Indes Néerlandaises 1907, No. 7, p. 1; Report of Schimmel & Co. November 1908, 19.

[2]) Recueil trav. chim. des P.-B. 25 (1906), 44; Chem. Zentralbl. 1906, I. 842.

In another oil which Eyken had obtained with a yield of 1.3 p. c. from another fragrant wood from Makassar, also known as *Kajoe garoe*, the botanical origin of which is unknown, he found guajol.

Family: TILIACEÆ.

477. Linden Flower Oil.

This oil[1]) is obtained by extracting with ether the aqueous distillate of linden flowers after having been saturated with salt. Upon evaporation of the ether 0.038 p. c. of oil remain. Linden flower oil is colorless, very limpid, fairly volatile and possesses the odor of the fresh flowers to a high degree. In ether and alcohol it is soluble in all proportions.

The only known constituent of the oil is farnesol[2]), $C_{15}H_{24}O$ (see vol. I, p. 399), an aliphatic sesquiterpene alcohol, the constitution of which has been revealed by M. Kerschbaum[3]), C. Harries and R. Haarmann[4]).

Family: MALVACEÆ.

478. Oil of Marshmallow.

From marshmallow flowers, *Althæa officinalis*, L. (family *Malvaceæ*), H. Hænsel[5]) obtained upon distillation 0.024 p. c. of a concrete oil that melted at + 36° and possessed a honey-like odor.

The oil distilled from the leaves[6]) (yield 0.022 p. c.) was brown in color and had an acid odor. d_{20° 0.9209; A. V. 88.7; E. V. 33.9. Upon saponification an acid melting at 62° (palmitic acid) was obtained.

[1]) Winckler, Pharm. Zentralbl. 1837, 781.
[2]) Haarmann u. Reimer, D. R. P. 149603; Chem. Zentralbl. 1904, I. 975.
[3]) Berl. Berichte 46 (1913), 1732.
[4]) *Ibidem* 1737.
[5]) Pharm. Ztg. 47 (1902), 74.
[6]) Apotheker Ztg. 24 (1909), 283.

479. Oil of Ambrette Seeds.

Oleum Abelmoschi seminis. — Moschuskörneröl. — Essence de Graines d'Ambrette.

Origin. Ambrette seeds, which were official formerly as *Semen Abelmoschi* or *Grana moschata,* and which are no longer used in medicine but in perfumery, are obtained from *Abelmoschus moschatus,* Mœnch (*Hibiscus Abelmoschus,* L., family *Malvaceæ*). The herbaceous plant is indigenous to East India, but since some time is being cultivated in Java and the West Indies (Martinique) [1]).

This oil was first prepared by Schimmel & Co. [2]) in 1887. Upon distillation the comminuted ambrette seeds yield from 0.2 to 0.6 p.c. of oil.

Properties. Ordinary ambrette seed oil is a concrete mass resembling orris oil. Melting and congealing point increase with its fatty acid content. $d_{40°}$ about 0.891; $d_{80°}$ about 0.883; A.V. 75 to 140; E.V. 70 to 130.

Liquid ambrette seed oil which was introduced into commerce by Schimmel & Co. in 1902, is free from the odorless, hence valueless and for the most part objectionable, fatty acid. $d_{15°}$ 0.905 to 0.917; α_D slightly dextrogyrate, up to $+1°20'$, or rarely lævogyrate, up to $-2'24'$; $n_{D20°}$ 1.474 to 1.480; A.V. 0.8 to 2.5; E.V. 137 to 190; soluble in 2.5 to 8 vol. and more of 80 p.c. alcohol. An oil with an original ester value of 167.4, after acetylation yielded an ester value of 199.7.

In one instance somewhat deviating constants were obtained: $d_{15°}$ 0.9298; α_D $-1°34'$; $n_{D20°}$ to 1.48519; A.V. 0.7; E.V. 139.8; with 10 vol. of 80 p.c. alcohol no clear solution was obtained, soluble however in 0.5 vol. and more of 90 p.c. alcohol [3]).

Composition. *Farnesol,* $C_{15}H_{24}O$ [4]) (comp. vol. I, p. 416) is the only known constituent of ambrette seed oil. In the aqueous dis-

[1]) For the cultivation of the plant see Journ. d'Agriculture tropicale 5 (1905), 17; Report of Schimmel & Co. April 1905, 9.

[2]) Bericht von Schimmel & Co. 1887, 35; April 1888, 29; Report of Schimmel & Co. October 1898, 50; October 1902, 9; April 1912, 24.

[3]) Report of Schimmel & Co. April 1914, 30.

[4]) Haarmann u. Reimer, D.R.P. 149603; Berl. Berichte 46 (1913), 1732.

tillate *furfurol*[1]) has been found. The bulk of the ordinary ambrette seed oil is *palmitic acid* (m. p. 61°; elementary analysis of the silver salt[2])).

Family: STERCULIACEÆ.

480. Cacao Oil.

Formerly it was supposed that the odoriferous principle of cacao (*Theobroma Cacao*, L., family *Sterculiaceæ*) was identical with cacao red or closely related thereto. This, however, is not the case. Cacao red is absolutely odorless whereas the characteristic cacao odor is due to a volatile oil. Upon distillation of fermented cacao, J. Sack[3]) obtained traces of a volatile oil which was formed during the fermentation process. J. S. Bainbridge and S. H. Davies[4]) have subjected this oil to a more careful examination. Upon distillation of 2000 kg. of cacao beans they obtained 24 g. (0.001 p. c.) of an oil, part of which was contained originally in the beans, and part of which was probably generated during the process of fermentation and absorbed by the beans. This product consisted almost exclusively of esters of the lower fatty acids. Constants of the total oil: d_{15}. 0.9075; n_{D20} 1.4728. The presence of the following free acids was ascertained: *valeric* acid (elementary analysis), a mixture of *caprylic* and n-*caprinic* acids (analysis of the silver salt of the acid mixture), and probably *capronic* acid. Traces of a nitrogenous substance with an unpleasant odor were isolated with the aid of sulphuric acid. Primary alcohols were not present (the calcium chloride, with which the oil was dried, retained no alcohols). The following esters were obtained: *amyl acetate, amyl propionate,* and *amyl butyrate,* possibly also *hexyl butyrate* and *hexyl propionate.* *d*-Linalool is the principal constituent (more than 50 p. c.) of the oil originally contained in the beans. (b. p. 87 to 97° under 15 to 11 mm. pressure; d_{15}. 0.8936; $[\alpha]_{D20}$. $+ 11°36'$; n_{D20}. 1.4658.) Its phenylurethane melted at 60 to 61'.

1) Report of Schimmel & Co. October 1899, 36.
2) Observations made in the laboratory of Schimmel & Co.
3) Inspectie van den landbouw in West-Indië. Bull. No. 10, January 1906, p. 10.
4) Journ. chem. Soc. 101 (1912), 2209.

Family: THEACEÆ.

481. Tea Oil.

Upon extraction of dried tea leaves (*Thea chinensis*, Sims; *Camellia Thea*, Lk., family *Theaceæ*) with ether 0.6 to 0.98 p. c. of a lemon-yellow extract is obtained, which congeals upon cooling, possesses a decided odor of tea and tastes like tea. G. J. Mulder[1]) has erroneously designated this extract as the ethereal oil of tea for the bulk of this product consists of non-volatile extractive matter. Upon distillation of dry tea leaves Mulder obtained a milky aqueous distillate but no oil.

Genuine tea oil has been prepared by P. van Romburgh[2]) upon distillation of freshly fermented tea leaves. The yield amounted to 0.006 p. c.

Apparently the oil results during the process of fermentation and may be the product of the action of an enzyme similar to that of laccase upon a glucoside. The tea oil thus obtained has a specific gravity of 0.866 at 26°; angle of rotation (200 mm.) 0° 11'.

Upon repeated refractionation there was obtained a liquid which boiled at 153 to 154° (740 mm.), and had a penetrating fusel-like odor reminding of tea. The principal constituent is an *alcohol* of the formula $C_6H_{12}O$, the acetic ester of which boils at 160 to 165°.

Oxidation with potassium bichromate converted the alcohol into an oil of the composition of butyric acid. When heated with hydrochloric acid in a sealed tube to 100°, the alcohol yielded a chloride boiling at 120°.

Fraction 200 to 225° of tea oil consists of *methyl salicylate*.

The aqueous distillate contains *methyl alcohol* (b.p. 66°; nitro methyl-*m*-phenylene diamine compound m. p. of oxalic acid ester 51°). This alcohol, however, is not a product of the

[1]) Poggendorff's Annalen der Physik 43 (1838), 163. — Liebig's Annalen 28 (1838), 314.

[2]) Verslag Plantentuin te Buitenzorg 1895, 119 and 1896, 166; Report of Schimmel & Co. April 1897, 39 and April 1898, 50.

fermentation. As van Romburgh had previously pointed out, it is a constituent of the fresh non-fermented tea leaves.

The peculiar aroma of Chinese tea is added artificially, in large part, by mixing the tea leaves with aromatic flowers. However, after they have imparted their odor to the tea, the flowers are removed. Flowers of the orange family are principally used, also those of the *Olea fragrans,* occasionally those of *Magnolia* or of members of the *Anonaceæ*[1]).

From the young leaves of *Thea Sasangua* (Thunb.), Nois.[2]), a Japanese tree, H. Kimura[3]) obtained from 0.4 to 1 p.c. (computed with reference to the fresh material) of volatile oil, which had a 'brown or violet color and a sweetish odor. The young leaves that had grown in spring were finely cut, mixed with water and allowed to stand for 24 hours. Upon distillation with water vapor, this mixture yielded a milky distillate from which, after saturation with salt, the oil was shaken out with ether. If the leaves are stored for a longer period after having been picked they no longer yield a volatile oil. Properties: d_{21}, 1.0611; α_D + 0. The oil consists of about 97 p.c. eugenol (m. p. of benzoyl compound 68 to 70'), and contains an ester of an alcohol that has the pleasant odor of geraniol, also traces of a substance that reacts with bisulphite.

Family: GUTTIFERÆ.

482. Oil of St. John's Wort.

The flowering herb of *Hypericum perforatum,* L. (family *Guttiferæ*) yields, upon distillation with water vapor, 0.0928 p.c. of a volatile oil. d_{20} 0.8703; angle of rotation in a 25 mm. tube in 50 p.c. chloroform solution 1 10'; A. V. 23; S. V. 37[4]).

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[1]) Dybowski, Bull. de la chambre d'agriculture de la Cochinchine 11 (1908), 274.

[2]) According to the Index Kewensis this is synonymous with *Camellia Thea,* Lk.

[3]) Berichte d. deutsch. pharm. Ges. 21 (1911), 209.

[4]) H. Hænsel, Apotheker Ztg. 20 (1905), 45.

Family: DIPTEROCARPACEÆ.

483. Borneo Camphor Oil.

Origin and Production[1]). The Borneo camphor tree, *Dryobalanops aromatica*, Gärtn. *(D. Camphora,* Coleb., family *Dipterocarpaceæ)* is a forest giant indigenous to the northwest coast of Sumatra and northern Borneo. In the crevices and cracks of the trunks of older trees the highly prized Borneo camphor, also called Baros camphor, Sumatra camphor or Malay camphor, is found. The Malays, who designate it *Kayu kapur*[2]), use it for the embalming of their dead also for other ritual purposes and pay a high price therefore. In addition to this camphor the trees contain a volatile oil which is obtained either by tapping the trees or by the distillation of the wood.

In the forests only individual trees are to be found[3]); in groups of 20 to 40 forest trees only one may prove to be a Borneo camphor tree. Furthermore, but one out of a hundred of these contain borneol crystals, the presence of which is not indicated by any external signs. In order to detect the presence of these crystals they have to be chopped into; if odorless, the trees are allowed to remain standing, but not infrequently trees are met with that have been thus tested three or four times at points one above the other. Trees standing in the neighborhood of rivers are cut into logs, rafted to Sandakan, and converted into lumber. The wood is highly esteemed for building purposes, since it is less subject to attack by white ants than other lumber. Wood with a strong scent is converted into clothes chests, as the borneol keeps insects away.

J. M. Janse[4]) is of the opinion that he has found an explanation for the fact that some trees contain solid borneol, others only

[1]) As to the history of Borneo camphor, under camphor oil, vol. I, p. 124. Detailed accounts will also be found by J. Giglioli, *La canfora italiana,* Roma 1908, p. 18, also O. Beccari, *Nelle foreste di Borneo.* Firenze 1902.

[2]) M. Moszkowski, Notizbl. bot. Gart. Berlin-Dahlem 5 (1908), 82.

[3]) Special Consular Reports, Vol. XLIII, Part III, p. 6. Washington 1910.

[4]) Annales du Jardin botanique de Buitenzorg, second series, suppl. III. 1910, 947.

volatile oil. The trunks are at times inhabited by larvæ, probably those of beetles, which bore their passages through the wood. In these the volatile oil collects. If conditions are favorable, the borneol may sublime into crevices provided there are such.

The question of the presence of borneol in the Borneo camphor trees cultivated in the Botanical Garden at Buitenzorg had previously been investigated[1]). The segregation of borneol in the wood of felled trees could not be observed. However, a white substance, consisting principally of borneol, was found in holes bored into living trees.

The collection of Borneo camphor is a laborious and time-consuming task, which is performed by the natives with the observance of certain ceremonies. These have been described in detail by W. H. Furness[2]), who made a detailed study of the habits of the headhunters of Borneo.

When the Kayans start on an expedition for trees, in which they hope to find the highly prized camphor, they pay great attention to certain outward circumstances, which are interpreted as either a good or bad omen, for the success of the venture. If certain birds fly across their path from right to left, their chances are poor. If, however, these birds fly in the opposite direction, they regard this as a good omen. It is only under these favorable circumstances that they continue their expedition. However, before they can begin with their real task they must hear a barking deer, also kill a certain snake. After all these events have occurred they may hope for rich reward. They next stretch a rattan across the river near which the camphor trees are located and suspend from it wooden images, and models of their weapons, and wooden wedges, which are used for cleaving the felled trees. These serve as a sign to other camphor seekers that the river is blocked. Near to the trees to be chopped down they then build their hut. If, when the first blows of the axe resound, the cry of an omen bird is heard, they give up work for that day and sit idle away their time in their hut. When all signs are favorable and if the

[1]) *Verslag omtrent de te Buitenzorg gevestigde technische Afdeelingen van het Departement van Landbouw 1905.* Batavia 1906, p. 46 and 63.

[2]) E. Kremers, Pharm. Review 23 (1905), 7.

tree in question proves sufficiently rich in camphor, they plant near their hut a stake, whereof the outer surface has been cut into curled shavings and tufts down the sides and at the top. When the camphor tree has been felled, the trunk is cut into small pieces, and during this process the searchers are clad in their most showy war-clothes and armed with parang and spear. The searchers seem to regard the tree as a fallen foe, who can be made to yield his hidden treasure only at the point of sword and spear. The search for the crystals is tedious work; each piece of wood must be split with the greatest care and examined with minuteness. Trees containing crystals are commonly those with cavities. Up to 20 ft. above the roots no crystals are found. In addition to these much oil occurs. The blossoms possess a strong camphor odor. While in search of camphor, many of the Borneo tribes employ a peculiar camphor language, which is strictly observed by the *Malanaus* for they believe that the camphor crystals vanish when they use any other. It is probable that this camphor dialect reveals remnants of an old language. This peculiar custom persists everywhere in Borneo and the Malay peninsula. The choicest grade of camphor consists of translucent crystals three-fourths of an inch in length, for which a price of from 40 to 50 dollars per pound is paid in the uplands. The Punans are the principal collectors of camphor. Either they are engaged as guides by the *"Kayans, Kenyahs, Sibops"* or *"Ibans"*, or they gather the camphor themselves and trade it with neighboring tribes who, in turn, dispose of it to the Chinese. The yield of a single tree is said to vary between 3 and 11 pounds. The collected material is sorted into three grades: the largest and purest crystals are regarded as the best, the smallest are gray and pulverulent. With the high price paid for this drug in the East, it does not enter European commerce. An explanation for the high price paid in the Orient is found in the religious use made of the Borneo camphor.

An official Dutch publication[1]) dealing with camphor trees, apparently pertains also to the Borneo camphor tree. According to it 108.700 acres of primitive forest in Pahang (Malacca) are

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[1]) Handelsberichten (Den Haag) 7 (1913), 771.

reserved for camphor production. The camphor trees occur only in the higher altitudes of the forest. It is estimated that only one per cent. of the trees contain camphor crystals. The Sokais who inhabit this forest have not collected camphor for so long a period that they have forgotten the "camphor language" employed by their forefathers in the collection of camphor. Only the chief of the tribe, the *Pengkulu Kapur*, is supposed to be capable of judging whether a tree contains camphor or not. He detects its presence by the sense of smell after an incision has been made into the tree, and only after he has determined the presence of camphor crystals may a tree be cut down.

According to the data of the customs bureau[1]) the following amounts of Borneo camphor from British North Borneo were exported from Sandakan:

1908 . . . . 1162² ; lbs.   valued at $ 18.271. ($ 15.71 per lb.)
1909 1844   „   „   „ $ 21.037. ($ 11.41 „ „)

The independent states Sarawak and Brunei also produce Borneo camphor but no data are available either as to production or export. However, the trees are more numerous and are exploited according to the same methods prevailing in Borneo.

Properties. According to Macewan[2]) Borneo camphor oils of former days were occasionally colored green because of the presence of copper. The density of the liquid varied from 0.882 to 0.909. An oil which was subjected to chemical examination by Schimmel & Co.[3]) and which had been obtained from Singapur, was characterized by the following properties: color dark brown; d_{15} 0.9180; $\alpha_D + 11°5'$; n_{D20} 1.48847; soluble, with slight turbidity, in 5 vol. and more of 90 p.c. alcohol; A. V. 5.6; E. V. 0; E. V. after acetylation 50.5, corresponding to 17.67 p. c. of ester $C_{10}H_{17}O \cdot COCH_3$. Its odor was turpentiny, reminding at the same time of borneol. An oil distilled from leaves gathered in Buitenzorg revealed the following properties: d_{26} 0.8585; $[\alpha]_{D26} + 2°29'$[4]).

[1]) Special Consular Reports Vol. XLIII, Part III. p. 6, Washington 1910.
[2]) Pharmaceutical Journ. III. 15 (1885), 795, 1045.
[3]) Report of Schimmel & Co. April 1913, 32.
[4]) *Verslag omtrent de te Buitenzorg gevestigde technische Afdeelingen van het Departement van Landbouw 1905.* Batavia 1906, p. 46 and 63.

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[1]) Handelsberichten (Den Haag) 7 (1913), 771.

The same conclusion was arrived at by Schimmel & Co.[1]), who investigated an oil from Singapur, the constants of which have already been recorded under Properties.

After distillation over sodium, the first fraction (b. p. 155 to 156'; $d_{15°}$ 0.8631; $\alpha_D + 7°32'$; $n_{D20°}$ 1.46668) yielded a nitrosochloride (m. p. 103°) and a benzylamine base melting at 123 to 124°. Hence, this fraction contained d-α-pinene.

Hydrated with glacial acetic acid-sulphuric acid mixture, a fraction coming over at the boiling point of *camphene* ($d_{15°}$ 0.8639; $\alpha_D + 5°37'$) yielded a large amount of *iso*borneol, which, even after having been purified repeatedly by means of petroleum ether, however, melted as low as 208°.

Small amounts of *β-pinene* were contained in fraction 163 to 167° ($d_{15°}$ 0.8607; $\alpha_D - 0°20'$; $n_{D20°}$ 1.47102). Oxidized with permanganate, it yielded nopinic acid melting at 124 to 125'. Oxidized farther with permanganate the sodium salt yielded nopinone the semicarbazone of which melted between 186 and 188°.

Neither p-cymene, nor phellandrene were present in the oil.

Dipentene, however, could readily be identified in fractions 175 to 178' ($d_{15°}$ 0.8572; $\alpha_D - 6°36'$) for, upon bromination in glacial acetic acid solution, it yielded the tetrabromide melting at 125 to 126°.

In the higher boiling portion (55 to 85° under 5 mm. pressure) d-*borneol* was present. During another fractionation it solidified in the cooler. The remaining liquid, when tested with semicarbazide, proved to be free from camphor. Recrystallized from petroleum ether the borneol had the required melting point of 204°. Its chloroformic solution was dextrogyrate.

In order to remove the borneol from the higher fractions, also from the mother liquids, these were benzoylated with benzoyl chloride in the presence of pyridine. The non-esterified portion of the oil, after distillation with steam, consisted chiefly of l-α-*terpineol* melting at 35° (m. p. of phenylurethane 112°). Saponification of the steam-distilled residue yielded no other alcohols than borneol. The highest boiling fractions (b. p. 102 to 112° under 4 to 5 mm. pressure) consisted exclusively of sesquiterpenes. A hydrochloride, however, could not be obtained.

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[1]) Report of Schimmel & Co. April 1918, 32.

According to this investigation the oil contained about 35 p.c. terpenes, *viz.*, d-*α-pinene*, *β-pinene* and *dipentene*; about 10 p.c. of alcoholic constituents, *viz.*, *borneol* and *α-terpineol* (m. p. 35˚); about 20 p.c. *sesquiterpenes*; and approximately 35 p.c. *resin.*

484. Gurjun Balsam Oil.

Gurjunbalsamöl.   Essence de Baume de Gurjun.

Origin and Production. Gurjun, Gurjan, Gargan or Gardjan balsam, also erroneously known in commerce as East Indian copaiva balsam, is designated "wood oil"[1] in India. It has there been known for a long time and is used in considerable amounts as varnish.

Similar to turpentine, gurjun balsam is obtained from a variety of species of *Dipterocarpus* (family *Dipterocarpaceæ*) of which about fifty are known in southern and eastern Asia[2]. The *Dipterocarpaceæ* are among the most stately trees of the Indian mountain forests. A fullgrown trunk yields as much as 180 liters of balsam during a single summer.

In British East India two kinds of related balsams are differentiated; the *Kanyin* oil, which presumably is to be regarded as true gurjun balsam, and *In* oil.

Of the eight species which occur in the forests of Burma[3], *Dipterocarpus alatus*, Roxb., *D. lævis*, Ham.[4] and *D. turbinatus*, Gærtn.[4] yield *Kanyin* oils, whereas *D. Griffithii*, Miq., *D. incanus*, Roxb., *D. obtusifolius*, Teysm., *D. pilosus*, Roxb. and *D. tuberculatus*, Roxb., are supposed to yield *In* oils. The principal representatives of these two groups are *D. turbinatus*, Gærtn., for *Kanyin* oil and *D. tuberculatus*, Roxb., for *In* oil. . The two kinds of balsam differ appreciably both as to physical and chemical properties. This difference is due partly to the differences in the methods of production. Whereas the *Kanyin* oils are produced with the aid of fire, the *In* oils are collected without its applica-

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[1] This should not be confounded with the Chinese wood oil, a fatty oil from the seeds of *Aleurites cordata*, Steud. (family *Euphorbiaceæ*).

[2] Comp. D. Hanbury, Science Papers, 1876, p. 118.

[3] Oil, Paint and Drug Reporter 73 (1908), No. 13, p. 41.

[4] *D. lævis*, Ham. and *D. turbinatus*, Gærtn. are synonyms according to the Index Kewensis.

tion. The former are limpid and brown to greenish-black in color; the latter consist of thick, grayish to grayish-white exudates.

The production of the *Kanyin* oils is simple and crude. During the months of November to May one or several boxes (inverted pyramids), according to the thickness of the trunk, are cut into the trunk not far above the ground and the surface of the boxes burnt with the aid of torches. Once or twice each week the exuded balsam is removed with the aid of spoons. The surface is burned again and scraped in order to keep the pores open. A tree six feet in circumference with but a single box produces annually about 20 lbs. of balsam, valued on the spot at about 2 rupees per lb.

The *In* oils are produced in similar manner, but during the months from August to March. However, the application of fire is avoided. The surfaces of the boxes are repeatedly rasped in order to facilitate the flow of the sap. The yield of *In* oils is the same as that of the *Kanyin* oils. The *In* oils are used principally as varnishes, lacquers and in medicine and but rarely in the manufacture of torches.

The principal English places of export for gurjun balsam are Chittagong, Singapur, Moulmein in Tenasserim and Ak-yab in Arakan.

In similar manner the production of the balsam is conducted in Cochin China where it is known as *Huile de bois*[1]). In spring, a hole is bored into the trunk at an angle of 45°. At the opening a large cavity is dug out of the trunk for the reception of a vessel into which the balsam is allowed to flow. When the exudation begins, several burning coals are placed into the cavity to induce the downward flow of the balsam. The exudation continues for about six months. The balsam collected during the dry season is the better. The average yield is 80 liters, but exceptional trees have yielded 200 liters and more.

In Cochin China there are principally four markets, *viz.*, Tayninh, Thudaumot, Choben and Taymit. Saigon is the place of export.

According to its source and method of production, gurjun balsam varies as to consistence, color and behavior toward solvents. Viewed by reflected light the better grades are greenish-

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[1]) Revue de la Droguerie; Journ. de Parfum. et Savonn. 18 (1905), 2.

gray, somewhat turbid and slightly fluorescent; viewed by trans-
mitted light they are perfectly clear and reddish-brown. Odor
and taste remind of copaiva balsam. Specific gravity 0.95 to 0.97;
α_{D} – 23 to – 70'; $n_{D20°}$ 1.510 to 1.516.

Steam distillation yields about 60 to 75 p.c. of oil.

Properties. The oil of gurjun balsam is a yellow, somewhat
thickish liquid, sp. gr. 0.918 to 0.930. The angle of rotation α_{D}
varies between – 35 and 130', hence is frequently as high as is
but rarely observed in a volatile oil. $n_{D20°}$ 1.501 to 1.505; A.V.
up to 1; E.V. up to 8; E.V. after acetylation (2 determinations)
6 to 10. Most of the balsams yield lævogyrate oils; however,
strongly dextrogyrate oils have been observed[1]) and in one ins-
tance an inactive oil[2]). In 90 p.c. alcohol the oil is not com-
pletely soluble; even in 95 p.c. alcohol, of which from 7 to 10 vols.
are required solubility is not unlimited.

Of special interest are the properties of two oils obtained
from balsams the botanical source of which were definitely known.
They were sent to Schimmel & Co.[3]) by Mr. C. G. Rogers, Con-
servator of Forests, of Rangoon.

One of these balsams obtained from *Dipterocarpus turbi-
natus*, Gærtn. fil.[4]) is known as *Gurjan oil* in Burma, Bengal
and in Andaman islands. It was a slightly acid (A.V. 10.9), milky
liquid, sp. gr. 0.9811 at 15'. Upon standing, particularly in a warm
place, it separated into a brown oil which floated on the surface,
and a tough, grayish-white, emulsion-like mass. The oily layer
had the following properties: $d_{15°}$ 0.9706; α_{D} – 10°8'; $n_{D20°}$ 1.51200;
A.V. 7.3; E.V. 1.9. Distilled with water vapor, the total balsam
yielded 46 p.c. of light yellow oil of a balsamic odor which re-
vealed the following properties: $d_{15°}$ 0.9271; α_{D} – 37°; $n_{D20°}$ 1.50070;
A.V. 0; E.V. 1.9; soluble in 7 vol. and more of 90 p.c. alcohol.

Very different in appearance was the second balsam that
had been obtained from *Dipterocarpus tuberculatus*, Roxb.[5]).

[1]) Dymock, Warden and Hooper, Pharmacographia Indica. 1890, vol I, p. 193.

[2]) A. Tschirch and L. Weil, Arch. der Pharm. 241 (1903), 382.

[3]) Report of Schimmel & Co. April 1913, 67.

[4]) Comp. also R. S. Pearson, Commercial guide to the forest economic
products of India. Calcutta 1912, p. 140.

[5]) Comp. also R. S. Pearson, Commercial guide to the forest economic
products of India. Calcutta 1912, p. 140.

In Borneo it is known as *In oil* and there plays a subordinate role as compared with the *Gurjan oil*. The light brownish balsam is of the consistence of turpentine; sp. gr. 1.029; A.V. 17.8; E.V. 0. The oil, obtained by steam distillation with a yield of 33 p..c., was yellowish-brown and soluble in 6 vol. and more of 95 p. c. alcohol. d_{15} 0.9001; α_D —99° 40'; $n_{D20°}$ 1.50070; S. V. 0. When tested by means of Turner's test (vol. II, p. 597) both balsam and oil yielded the characteristic color reaction.

Composition. As ascertained by Flückiger[1]) and others, gurjun balsam oil consists for the most part of sesquiterpenes, fairly uniform as to boiling temperature. Thus Schimmel & Co.[2]) observed that of an oil 86 p. c. distilled between 260 and 265° under ordinary pressure (741 mm.) and 6 p. c. between 265 and 269 . The sesquiterpenes, which have been examined more carefully by E. Deussen and H. Philipp[3]), have been designated gurjunenes by them. After repeated fractionation, one oil (d_{17}0.922; α_{17} —44°25') was resolved into a number of fractions boiling from 124³/₁ to 138³/₄ (12 mm.) and varying in their optical rotation from — 61 to $+ 1°$. The lowest fraction consisted of a hydrocarbon named *α-gurjunene* and the hydrocarbon of the higher boiling fractions *β-gurjunene*. α-Gurjunene boils at about 119' (12 mm.) and is strongly lævogyrate. The molecular refraction revealed its tricyclic character. β-Gurjunene boils at 122.5 and 123.5° (12 mm.), is slightly dextogyrate, and dicyclic. Upon oxidation of both hydrocarbons in acetone solution a ketone (?) $C_{15}H_{24}O$ is obtained. Regenerated from its semicarbazone (m. p. 234°) it revealed the following constants; b. p. 175 to 178° under 12 mm.; d 1.0160; $\alpha + 120$ to $+ 130°$; n_D 1.5303; b. p. of the oxime 204 (12 mm.).

If an ethereal solution of rectified gurjun balsam oil, *i. e.* a mixture of α- and β-gurjunene is saturated with hydrogen chloride gas and the mixture set aside at room temperature for two days, there results, after splitting off the hydrogen chloride by means of sodium acetate, a bicyclic hydrocarbon (b. p. 129.5 to 132 under 12 mm. pressure; d 0.9183; n_D 1.5057) which the authors designate iso*gurjunene*.

[1]) Flückiger, *Pharmakognosie*, 3rd ed., p. 102. Comp. also C. Werner, Zeitschr. f. Chem. und Pharmacie 5 (1862), 588; Jahresb. f. Chem. 1862, 461.

[2]) Report of Schimmel & Co. April 1909, 56.

[3]) Liebig's Annalen 869 (1909), 56; 374 (1910), 105. — Chem. Ztg. 84 (1910), 921.

The sesquiterpenes of gurjun balsam oil have also been studied by F. W. Semmler, K. E. Spornitz and W. Jakubowicz[1]). They found that crude gurjunene consists of about 67 p. c. of strongly *lævogyrate tricyclene-gurjunene* (α-gurjunene) and about 33 p. c. of strongly *dextrogyrate tricyclogurjunene* of the cedrene type (β-gurjunene). In order to obtain the latter in a pure condition, the glacial acetic acid solution of the crude gurjunene was treated with chromic acid, during which process the original lævorotation ($\alpha_D - 55$) is changed to dextrorotation. By repeated oxidation, finally with potassium permanganate in acetone solution, a fraction was obtained, which, after distillation over sodium, boiled between 120 and 123° under 13 mm. pressure (d 0.9348; $\alpha_D + 74.5$; n_D 1.50275) and consisted of pure dextrogyrate tricyclic gurjunene of the cedrene type (tricyclogurjunene). Upon oxidation of this sesquiterpene either with chromic acid or potassium permanganate, there resulted a very good yield of the gurjunene-ketone of Deussen and Philipp. The ketone regenerated from the semicarbazone (m. p. 237) melts at 43 (b. p. 163 to 166" under 10 mm. pressure; d_{20} 1.017; $\alpha_D \cdot 123$; n_D 1.52700). Semmler and his co-laborers assume that gurjunene-ketone has the formula $C_{15}H_{22}O$ and not $C_{14}H_{24}O$, as recorded by Deussen and Philipp, although the molecular refraction agrees better with the formula $C_{15}H_{24}O$; computed for $C_{15}H_{22}O_1$ 64.63; found 65.90; increment 1.27. Reduced with sodium and alcohol, the ketone yields gurjunene alcohol, $C_{15}H_{24}O$ (m. p. 104°; b. p. 155 to 159 under 11 mm. pressure; d 1.001; $\alpha_D + 34$°; n_D 1.51859). The ketone could not be reduced farther. Upon the reduction of tricyclogurjunene with platinum and hydrogen only two atoms of hydrogen were added with the formation of tricyclodihydrogurjunene (b. p. 120' under 8 mm. pressure; d 0.9258; $\alpha_D - 37.5$°; n_D 1.49775). Tricyclogurjunene was also obtained when gurjunene-ketone semicarbazone was heated in a sealed tube with sodium alcoholate and alcohol to 160°. The hydrocarbon thus obtained revealed the same constants as the original hydrocarbon with the exception of the optical rotation which had been lowered. That the hydrocarbon in question was tricyclogurjunene, though partly inverted, became apparent from the observation that upon

¹) Berl. Berichte 47 (1914), 1029, 1141.

oxidation with potassium permanganate gurjunene ketone resulted once more. Like all sesquiterpenes that show a similarity to cedrene, tricyclogurjunene does not give Turner's color reaction. Fractional distillation of the crude gurjunene yielded a sesquiterpene (b. p. 114 to 116° under 10 mm. pressure; d_{20}, 0.918; α_D,—95°; n_D, 1.5010) which proved to be relatively pure tricyclene-gurjunene (α-gurjunene). When reduced, only two atoms of hydrogen were added. Upon oxidation it yielded no gurjunene-ketone but gave the Turner color reaction to a marked degree. Reduced with platinum and hydrogen, crude gurjunene added but two hydrogen atoms, from which observations the authors conclude that it cannot contain bicyclic terpenes.

DETECTION OF GURJUN BALSAM OIL. On account of its feeble odor, gurjun balsam oil is a dangerous adulterant of other volatile oils. However, because of its high boiling point, its high optical rotation and the sparing solubility in alcohol, its detection affords no great difficulties. For the detection of gurjun balsam oil in rose oil and in copaiba balsam oil see vol. II pp. 575 and 598 respectively.

485. Balao Balsam Oil.

In the Philippines several species of *Dipterocarpus* yield socalled "wood oils" which are similar to gurjun balsam and are produced in like manner. *Balao* balsam[1]), which finds general application in the Philippines is obtained from *Dipterocarpus grandifluus,* a tree designated *Apitong* by the natives.

The balsam which is a mixture of solid resin, water and from 25 to 40 p. c. of volatile oil, is used for pitching boats, or as a lacquer for wood, for which purpose it is mixed with solid resin or lime. It is also used for illumination purposes. For its production, a cup-shaped cavity is hewn into the trunk of the tree, from which the exudation is removed as needed. If the flow of the tapped tree is slow the latter is ignited. This increases the flow, but the product is colored dark thereby. The maximum amount yielded by a tree in a single day is 1 kg. The fresh oleoresin is white but soon assumes a dark color. In a thin layer it rapidly hardens. It does not constitute a

[1]) A. M. Clover, Philippine Journ of Sc. 1 (1906), A, 191.

homogeneous liquid and contains a large number of granules which do not dissolve but remain suspended in the liquid. Its odor is faint but characteristic. It is soluble in alcohol and all other solvents. It contains water which cannot readily be separated. Only after the balsam has been mixed with sesquiterpene-containing oil and heating the mixture on an oil bath to 140° is the water driven off. When heated appreciably higher a clear solution finally results, which again congeals partly upon cooling. The balsam behaves in like manner toward fatty oils, a property of considerable importance in the manufacture of lacquer. Whereas balao balsam is liquid at ordinary temperature, upon steam distillation it becomes so tough that only traces of a volatile oil can be obtained. Neither can the volatile constituents be isolated by means of distillation under diminished pressure, since the mass foams from the very beginning and the dehydrated residue becomes hard. Hence it is necessary to distil over the direct flame whereby ultimately 50 p. c. of the balsam passes over, approximately one-half of which consists of oil, the other half of water. The boiling temperatures fluctuate between 250 and 300°, the bulk passing over between 260 to 264° (760 mm.) or 151 to 154° (40 mm.); $d_{30°}^{30°}$ 0.9127 to 0.9131; α_{D30} +78.5 to +87°. The distillate was faintly yellow and had the characteristic odor of *balao*.

From the oil prepared by distillation under atmospheric pressure and *in vacuo*, R. F. Bacon[1]) obtained a mixture of crystalline acids which were only partially soluble in ether; also a fraction boiling between 128 and 131° (13 mm.) in which he proved the presence of a *sesquiterpene*. Distilled three times over sodium a colorless oil with the following properties resulted: b. p. 261 to 262.4° (ord. pressure), 118 to 119° (8 mm.); $d_{1°}^{30°}$ 0.9104; $\alpha_{D30°}$ +116.4°; $n_{D30°}$ 1.4956; S. V. 0; mol. ref. found 65.9, computed for $C_{15}H_{24}/_2$ 66.15. Hence the sesquiterpene contains two cycles and two double bonds. Attempts to prepare characteristic oxidation products failed. Photochemically the sesquiterpene is sensitive to the extent that in a glass-stoppered bottle the angle of rotation was reduced to +101.2° after 1½ years. The other constants had not changed perceptibly.

¹) A. M. Clover, Philippine Journ. of Sc. 4 (1909), A, 121.

486. Malapaho Balsam Oil.

According to A. M. Clover[1]) *malapaho* balsam is likewise produced in the Philippines. Its source is *Dipterocarpus vernicifluus*, Blanco, a tree known as *Panao* by the natives. This balsam is not used as extensively as *balao* presumably because it does not dry as readily. Its manner of production is the same. The fresh balsam is white, viscid, and of characteristic odor which enables its differentiation from similar products. It absorbs atmospheric oxygen and becomes dark upon standing. However, even in thin layer it solidifies with difficulty. At 100' it becomes more liquid and thus differs from *balao*. It is soluble in ether and chloroform with the separation of water. Furthermore, it is partly soluble in alcohol and benzene. None of its constituents is soluble in water. Distilled over a direct flame, it behaves like *balao* balsam. All samples contained water (abt. 25 p. c.), sesquiterpene-containing oil (abt. 35 p. c.), and solid (non-volatile) constituents (abt. 40 p. c.). The sesquiterpene boils almost completely between 256 and 261 (760 mm.); $d_{30°}^{30°}$ 0.9165; α_{D30} — 54°.

487. Mayapis Balsam Oil.

Mayapis balsam is obtained from *Dipterocarpus anisoptera vidaliana*, a tree the habitat of which is restricted to the Philippines[2]). In its properties it is very similar to the two balsams previously described. A sample contained 15 p. c. water and 25 p. c. of sesquiterpene-containing oil. The residue consisted of hard rosin. The oil rectified in vacuum had a light yellow color; $d_{30°}^{30°}$ 0.9056; b. p. 132 to 140° (17 mm.).

488. Oil from Solid Lagam Balsam.

According to L. van Itallie and M. Kerbosch[3]) solid Lagam balsam is derived from *Dipterocarpus Hasseltii*, Bl. or *D. trinervis*, Bl., two related possibly identical *Dipterocarpaceæ*[4]). It

[1]) A. M. Clover, Philippine Journ. of Sc. 1 (1906), A, 198.
[2]) *Ibidem* 1 (1906), A, 201.
[3]) Arch. der Pharm. 250 (1912), 199.
[4]) The liquid Lagam balsam is derived from *Canarium eupteron*, Miq. (family *Burseraceæ*). See p. 139.

is produced in the interior of Sumatra. Upon distillation with water vapor, this balsam yielded from 10.5 to 22 p.c. of a volatile oil characterized by the following properties: d_{16} 0.9065; α_D - 8.9°; $n_{D16.5}$ 1.50029. It consists of *caryophyllene* (m. p. of the nitrosate 112 to 113°).

489. Dammar Resin Oil.

The bulk of the dammar resin now in commerce is derived from *Shorea Wiesneri*, Schiffn. (family *Dipterocarpaceæ*) and from closely related species.

Upon distillation of the resin, H. Haensel[1]) obtained 1.06 p.c. of a golden-yellow oil which was optically inactive; d_{21} 0.9352. It began to boil at 205°; up to 240°, 60 p.c. came over; up to 265° an additional 30 p.c.; the remainder resinified.

Family: CISTACEÆ.

490. Ladanum Oil.

Origin and Production. Ladanum or labdanum is a soft resinous mass which is obtained from several species of the genus *Cistus*, mostly from *C. creticus*, L. and from *C. ladaniferus*, L. (family *Cistaceæ*) in Crete. The sticky exudation of the glandular leaf adheres to the hairs of the skin and beard of the goats and is removed therefrom by means of a kind of comb. In Spain the twigs, more particularly of *C. ladaniferus*, are boiled with water and the resin which collects on the surface removed by skimming[2]).

Upon distillation of ladanum resin Schimmel & Co.[3]) obtained 0.91 p.c. of a golden-yellow oil with a strong but pleasant amber-like odor. Having stood for half a year handsome crystals separated constituting about one-fourth of the entire oil[4]).

Composition. According to H. Masson[5]) the oil contains two ketones. Fraction 85 to 90° (15 mm.) when treated with

[1]) Pharm. Ztg. 47 (1902), 819.
[2]) Comp. E. M. Holmes, Perfum. Record 2 (1911), 132, 155.
[3]) Report of Schimmel & Co. April 1898, 71.
[4]) *Ibidem* October 1898, 26.
[5]) Compt. rend. 154 (1912), 517.

hydroxylamine hydrochloride, yielded an oxime that boiled at 133´ (16 mm.). From this the ketone was regenerated, which, when purified by means of its semicarbazone (m. p. 207°) boiled at 200° (91° under 18 mm. pressure) and which, upon oxidation, yielded benzoic acid, thus proving its identity with *acetophenone*. The occurrence of this ketone in a volatile oil had not previously been recorded.

Fraction 70 to 78° (15 mm. pressure) likewise yielded an oxime melting at 106 (b. p. 126 to 127° under 17 mm. pressure), from which Masson regenerated a ketone $C_9H_{16}O$ which possessed the following properties; b. p. 178 to 179 (66 to 67° under 10 mm. pressure); $d_{0°}$ 0.922; $\alpha : 0°$; $n_{D28°}$ 1.4494. The ketone did not react with bisulphite. It yielded a monobromide melting at 41° and a semicarbazone melting at 220 to 221´. With sodium and moist ether it was reduced to the corresponding secondary alcohol, which formed large crystals melting at 51´ and boiling at 87° (28 mm.). Cold, 3 p.c. potassium permanganate solution oxidized the ketone to geronic acid (b. p. 190 to 191° under 31 mm. pressure; m. p. of semicarbazone 164°), which, upon further oxidation with sodium hypobromite, yielded bromoform and α,α-dimethyladipic acid. This "Abbau" proves that the ketone in question is the hitherto undescribed *trimethyl-1.5.5-hexanone-6*.
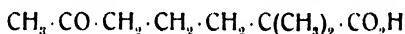
$$CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C(CH_3)_2 \cdot CO_2H$$
Geronic acid

In addition to these two ketones, the oil, according to Masson, contains phenols, esters and sesquiterpene derivatives.

According to an investigation of E. J. Emmanuel [1]) the occurrence of *guajol* in ladanum oil is not excluded.
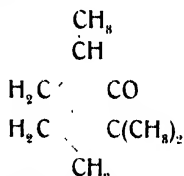
CH_3
CH
H_2C CO
H_2C $C(CH_3)_2$
CH_2
Trimethyl-1.5.5-hexanone-6.

491. Cistus Leaf Oils.

An oil distilled from the leaves of the *Cistus ladaniferus*, L. possessed an unpleasant narcotic odor. Its specific gravity at 13° was 0.925 and it boiled between 165 and 280° with formation of acetic acid [2]).

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[1]) Arch. der Pharm. 250 (1912), 111.
[2]) Bericht von Schimmel & Co. October 1889, 53.

An oil obtained from the fresh leaves was light yellow in color and possessed an exceedingly agreeable odor which clearly resembled that obtained from the resin, likewise reminding of ambra. Other properties: $d_{15°}$ 0.9223; $\alpha_D - 11°12'$; A.V. 5.31; E. V. 23.10; soluble in 0.5 vol. of 90 p.c. alcohol, upon addition of more alcohol turbidity results with the separation of paraffin[1]).

Two additional cistus leaf oils[2]) have been distilled by Schimmel & Co. from Spanish material. They also possessed an ambra-like odor, therein resembling that of ladanum oil.

OIL OF CISTUS MONSPELIENSIS, L.

Yield 0.015 p.c.; $d_{15°}$ 0.9786; $\alpha_D +1°40'$; A.V. 15.7; E.V. 31.51. Between 20 and 25° the light yellow oil separates *paraffin*, m. p. 64°, in abundance.

OIL OF CISTUS SALVIFOLIUS, L.

Yield 0.024 p.c.; $d_{15°}$ 0.9736; $\alpha_D + 17°20'$; A. V. 16.86; E. V. 22.73. The oil is yellowish-green and, like the previous one, separates *paraffin*.

Family: WINTERANACEÆ (CANELLACEÆ).

492. Canella Bark Oil.

White canella or cinnamon bark, also known as false Winter's bark, is obtained from *Canella alba*, Murr. *(Winterana Canella*, L., family *Winteranaceæ [Canellaceæ]),* indigenous to the Antilles and Florida.

Upon distillation of canella bark 0.75 to 1.25 p.c. of a volatile oil are obtained the odor of which reminds of that of a mixture of clove and cajeput oils. d 0.920 to 0.935. Optically it is slightly dextrogyrate, $\alpha_D + 1°8'$.

When shaken with alkali a phenol, *eugenol*[3]) (benzoyl eugenol[4])) could be removed.

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[1]) Observations made in the laboratory of Schimmel & Co.
[2]) Report of Schimmel & Co. October 1903, 22.
[3]) W. Meyer and von Reiche, Liebig's Annalen 47 (1843), 234.
[4]) Bruun, Proceed. Wisc. Pharm. Assoc. 1893, 36.

Upon fractionation of the non-phenol constituents the lowest portion came over between 165 and 170° (d 0.888; α_D — 3.38°). The preparation of the pinene nitrosochloride and of the pinene nitrolbenzylamine (m. p. 122 to 123°) proved this fraction to be l-*α-pinene*[1]). The next higher fraction consisted of *cineol*[2]) (m. p. of cineolic acid 197°)[3]). The highest fractions contain *caryophyllene*[1]), which was identified by means of its hydrate melting between 92 and 95°.

493. Karambusi Oil.

Upon distillation of the bark of the Karambusi tree *(Warburgia Stuhlmannii,* Engl., family *Winteranaceæ),* a native of East Africa with water vapor, W. Lenz[4]) obtained 0.6 p. c. of a thick, yellowish-red oil which, with reflected light, revealed a greenish fluorescence, and the odor of which resembled that of sandalwood oil. d_{20} 0.9864; $\alpha_{D20°}$ 41.2 ; $n_{D20°}$ 1.51269; S. V. 11.2; E. V. after acetylation 111.5; miscible with absolute alcohol; with an equal weight of 90 p. c. alcohol it formed a clear solution, but the addition of more alcohol rendered the solution turbid. Under 24 mm. pressure, it boiled between 100 and 102 . With sodium acid sulphite solution an aldehyde was extracted, but further information about its nature is wanting. In addition Lenz showed the presence of a small amount of sulphur compounds.

Family: VIOLACEÆ.

494. Oil of Violets.

The flowers of the fragrant violet *(Viola odorata,* L., family *Violaceæ)* do not yield a volatile oil upon distillation. For the production of this highly prized perfume the pomade or enfleurage method (see Vol. I, p. 258), or, in recent years more commonly the extraction method (see Vol. I, p. 247) is employed. The leaves of the violet are used in like manner.

[1]) R. T. Williams, Pharm. Rundsch. (New York) 12 (1894), 183.
[2]) Report of Schimmel & Co. October 1890, 66.
[3]) Bruun, Proceed. Wisc. Pharm. Assoc. 1893, 36.
[4]) Berichte d. deutsch. pharm. Ges. 20 (1910), 351.

Victoria violets[1]), when extracted with petroleum ether, yielded
1.5 to 1.8 p.c. of a concrete oil from which the volatile oil can
be obtained according to the method described on p. 252 of vol. I.

According to H. von Soden[2]), 1000 kg. of violet flowers
yielded 31 g. (0.0031 p.c.) of a faintly greenish oil without
fluorescence, which did not congeal in a freezing mixture.
d_{15} 0.920; $\alpha_{D15^{\circ}}$ + 104°15'; A. V. 10; E. V. 37; readily soluble in
alcohol. In its concentrated form the odor of the ethereal oil
of violets but little resembles that of the violet. Only after it
has been diluted in the ratio 1:5000 to 10000 the characteristic
violet odor, accompanied by an herbaceous bye-odor from the
calyces, becomes prominent. Oil of violets is the most costly
of the volatile oils used practically. Disregarding the cost of
manufacture, one kilo of the oil deprived of its odorless ad-
mixtures, would be worth $\$ 20000$.

495. Oil of Pansies.

Upon distillation, the freshly flowering plant, with root, of
Viola tricolor, L. (family *Violaceæ*) yielded but 0.00859 p.c. of
a volatile oil, which had a decided odor of wintergreen. Upon
saponification, the small amount of available oil yielded salicylic
acid (m. p. 156°) almost quantitatively, hence the oil seems to
consist almost exclusively of methyl salicylate[3]).

According to A. Desmoulière[4]), methyl salicylate is not con-
tained as such in the pansy, but in the form of a glucoside, which
in the presence of water and under the influence of an enzyme
is hydrolyzed to methyl salicylate and glucose. This glucoside,
presumably gaultherin, was obtained in amorphous condition only.

From the circumstance that the wintergreen odor is produced
only when the herb is crushed, Desmoulière concludes that
glucoside and ferment are contained in different cells and hence
cannot react on each other until brought together. Probably
similar conditions prevail in other *Violaceæ*, but Desmoulière's
observations apply only to the cultivated pansy.

[1]) In southern France several varieties are employed, more particularly
Parma violets, Victoria violets and Tzar violets.
[2]) Journ. f. prakt. Chem. II. 69 (1904), 261.
[3]) Report of Schimmel & Co. October 1899, 56.
[4]) Journ. de Pharm. et Chim. VI. 19 (1904), 121.

Family: TURNERACEÆ.

496. Damiana Leaf Oil.

Damiana leaves[1]), which have been used for medicinal purposes in the United States since 1875, are referred to several *Turnera* species, family *Turneraceæ*, more particularly to *T. diffusa*, Willd. and its variety *aphrodisiaca*, Ward. However, damiana leaves occur in commerce which are referable to other plants, e. g. *Bigelovia veneta*, Gray (*Aplopappus discoideus*, D. C.). To the diversity of source are due the differences in the volatile oils resulting from the several distillations.

F. W. Pantzer[2]), in 1887, obtained 0.5 p.c. of a yellow oil with an aromatic odor and a warm, camphor-like, bitter taste.

In one distillation, Schimmel & Co.[3]) obtained in 1888, 0.9 p.c. of a green, viscid oil of a chamomile odor, sp. gr. 0.970; boiling temperature between 250 and 310°. The highest boiling fraction had a blue color.

From another lot of leaves the same firm[4]) obtained, in 1896, 1 p.c. of an oil with the following properties: d 0.943; a_D, — 23°25'; S. V. 41.8. Upon standing in the cold a crystalline separation was observed at the surface resembling that which is found when rose oil begins to congeal. Hence it is probable that the oil contains paraffin.

Family: CARICACEÆ.

497. Oil of Carica Papaya.

The seeds of the melon tree, *Carica Papaya*, L. (family *Caricaceæ*), yield upon distillation a volatile oil which contains sulphur and nitrogen. The flowers have a taste reminding of that of cress. Like the stem and leaves, the roots, which also

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[1]) Comp. Damiana (The Mexican tea) by J. U. Lloyd, Pharm. Review 22 (1904), 126.

[2]) Americ. Journ. Pharm. 59 (1887), 69.

[3]) Bericht von Schimmel & Co. April 1888, 44.

[4]) Report of Schimmel & Co. April 1897, 15.

have a pungent taste, contain an enzyme and a mustard oil-yielding glucoside[1]). According to D. Hooper[2]) the seeds yield an allyl compound upon distillation.

Family: THYMELACEÆ.

498. Aquilaria Wood Oil.

The aloe wood derived from a species of *Aquilaria*, presumably from *A. malaccensis*, L. (family *Thymelaceæ*) is used in Java for perfumery purposes[3]). It is remarkably soft and white; however, when resinified it is hard and heavy like gonystilus wood[4]).

Upon distillation with water vapor a small amount of oil was obtained with an odor reminding of gonystilol[4]). ·A few crystals separated but the amount could not be increased, after purification of the oil, by inoculation with gonystilol, hence they are assumed to be different in composition.

Family: LYTHRACEÆ.

499. Henna Oil.

According to E. M. Holmes[5]), the flowers of the henna shrub, *Lawsonia inermis*, L. (family *Lythraceæ*), which are used for dyeing in the Orient, contain a volatile oil that has an odor of tearose.

Family: MYRTACEÆ.

500. Oil of Myrtle.

Oleum Myrti. — Myrtenöl. — Essence de Myrte.

Origin. The myrtle, *Myrtus communis*, L. (family *Myrtaceæ*) which is widely distributed in the rocky, mountainous regions of the Mediterranean, more particularly of Spain, Italy and

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[1]) L. Guignard, Journ. de Pharm. et Chim. V. 29 (1894), 412. -- C. Hartwich, Apotheker Ztg. 17 (1902), 340.

[2]) Pharmaceutical Journ. 91 (1913), 369.

[3]) W. G. Boorsma, Bull. dép. de l'agricult. aux Indes Néerlandaises 1907, No. 7, p. 1.

[4]) Comp. p. 158.

[5]) Pharmaceutical Journ. III. 10 (1880), 635.

southern France, is characterized by its fragrant flowers and leaves. For the production of the volatile oil[1]), the leaves only are used, giving a yield of about 0.3 p. c. commercial oil. Myrtle oil is, for the most part, of French and Spanish origin. More recently oils of other geographic source have entered commerce. The Corsican oil is especially prized.

Properties. Myrtle oil constitutes a yellow to greenish liquid of a pleasant, refreshing odor. Its properties, which vary somewhat with reference to the commercial varieties, are herewith tabulated[2]).

Oil from	d_{15°	α_D	n_{D20°	A. V.	E. V.	E. V. after acetyl.	Soluble
Spain . .	0.913 to 0.925	+22° to +25°20′	1.467 to 1.470	up to 1.7	68 to 86	103 to 117	in 1 to 2, rarely 5 vol. of 80 p. c. alcohol
France . .	0.890 to 0.904	+15 to +25	1.464 to 1.468	up to 1.8	19 to 43	38 to 56	in 0.5 vol of 90 p. c. alcohol, most oils are sol in 5 to 10 vol of 80 p. c. alcohol
Corsica	0.883 to 0.887	+22 to 27	1.464 to 1.470	up to 1.7	13 to 25	30 to 38	in 1, occasionally only in 2.5 vol. of 90 p. c. alc., insol. in 10 vol of 80 p c. alcohol.
Syria . .	0.893 to 0.922	+11 to +26	1.463 to 1.468	up to 5	18 to 31	54 to 72	in 1, occasionally only in 5 vol of 80 p. c alcohol
Asia Minor	0.913	+10 42′	1.467	1.5	39.4	94.9	in 0.9 vol and more of 80 p c alcohol
Cypres. .	0.917	8 11′	1.463	0.3	20.9	63.9	in 1 vol. 80 p. c. alcohol.
Algeria .	0.881 to 0.887	25°52′ to +27°30′	1.464	0.3 up to 1.1	17 to 20.6	39.2	in 0.5, occasionally only in 2.5 vol. and more of 90 p c alcohol.
Dalmatia .	0.925	+13 20′	1.466	1.0	134.8	186.7	in 5.2 vol of 70 p. c. alcohol.

Composition. Fraction 158 to 160 consists of a dextrogyrate terpene $C_{10}H_{16}$ ($[\alpha]_D + 36.8°$), the chemical behavior of which indicated pinene[3]). Its identity with *a-pinene* was established by the preparation of its nitrosochloride[4]). A fraction of the

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[1]) According to M. Raybaud (Journ. de Pharm. II. 20 [1834], 463; Pharm. Zentralbl. 1834, II. 932) the fresh fruits likewise contain volatile oil.

[2]) Report of Schimmel & Co., April 1902, 78; April 1909, 71; April 1910, 78; October 1911, 61; April 1912, 94.

[3]) The "myrtene" of Gladstone, Journ. chem. Soc. 17 (1864), 1 and 25 (1872), 1.

[4]) E. Jahns, Arch. der Pharm. 227 (1889), 174.

same boiling temperature ($a_{_D} + 36°$) was examined for camphene (treatment with glacial acetic acid and sulphuric acid) by Schimmel & Co.[1]). In one instance the crystals, after repeated recrystallization from petroleum ether, melted at 203 to 204°, in another at 205°. In neither case could the melting point be raised. This fact, as well as the appearance of the product, which clearly resembled borneol, indicated that it was not pure *iso*borneol, but a mixture of borneol and *iso*borneol. Treatment of the reaction product with diluted sulphuric acid gave no positive results and likewise indicated a mixture. Hence, all that can be said is that in the first fraction of myrtle oil there is a hydrocarbon which behaves like camphene. This does not exclude the presence of a third hydrocarbon which yields borneol when treated with glacial acetic acid and sulphuric acid.

The fraction that distilled about 176° contains *cineol*. Hydrogen chloride[2]), also hydrogen bromide[3]), yield the characteristic addition products which hydrolyze with water to pure cineol.

Fraction 180° consists of dipentene (m. p. of tetrabromide 125°). In the higher boiling fractions H. v. Soden and Fr. Elze[4]) have found a new alcohol of the formula $C_{10}H_{16}O$ which they named *myrtenol*. The alcohol occurs principally as acetic ester and was obtained from the ester fraction upon saponification with alcoholic potash. By converting the myrtenol into its acid phthalate m. p. 116°, it could be separated from the accompanying alcohols *geraniol* and *nerol*[5]). From its phthalate myrtenol was regenerated as a viscid, colorless oil of myrtle-like odor. B. p. 220 to 221° (751 mm.); 79.5 to 80° (3.5 mm.); $d_{15°} 0.985$; $a_{_D} 49°25'$. It can be acetylated quantitatively.

Its constitution (see vol. I, p. 391) has been revealed by F. W. Semmler and K. Bartelt[6]).

Formerly myrtle oil was used extensively for the preparation of "myrtol", as the fraction 160 to 180° was designated. The

[1]) Report of Schimmel & Co. April 1907, 73.

[2]) Jahns, *loc. cit.*

[3]) Bericht von Schimmel & Co. April 1889, 29.

[4]) Chem. Ztg. 29 (1905), 1031.

[5]) Fr. Elze, Chem. Ztg. 34 (1910), 857.

[6]) Berl. Berichte 40 (1907), 1363.

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Asia Minor	0.913	+10 42'	1.467	1.5	39.4	94.9	in 0.9 vol and more of 80 p.c. alcohol
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[1]) According to M. Raybaud (Journ. de Pharm. II. 20 [1834], 463; Pharm. Zentralbl. 1834, II. 932) the fresh fruits likewise contain volatile oil.

[2]) Report of Schimmel & Co., April 1902, 78; April 1909, 71; April 1910, 78; October 1911, 61; April 1912, 94.

[3]) The "myrtene" of Gladstone, Journ. chem. Soc. 17 (1864), 1 and 25 (1872), 1.

[4]) E. Jahns, Arch. der Pharm. 227 (1889), 174.

Allspice yields from 3 to 4.5 p. c. of volatile oil upon distillation, the early stages of which are accompanied by a strong development of ammonia.

Properties. Oil of pimento is yellow to brownish in color, of agreeable spicy odor, which reminds of that of cloves yet differs therefrom, and of a pungent taste. d_{15} 1.024 to 1.055; $\alpha_D - 0^\circ 40'$ to 5°; n_{D20° 1.525 to 1.534; soluble in 1 to 2 vol. and more of 70 p. c. alcohol, occasionally revealing opalescence and even turbidity upon dilution; phenol content 65 to 80 p. c., determined with 3 p. c. soda solution.

Composition. The experiments of Bonastre[1]), who prepared the alkali "salts" of the "acid" constituents of pimento oil, suggested that the similarity of this oil with that of cloves might·be due to the identity of the phenol in both. Proof of the identity of both phenols was brought by C. Oeser[2]) who isolated the eugenol by means of potassium hydroxide and analyzed it. The benzoyl derivative which was prepared later, melted at 69 to 70°[3]).

The non-phenol constituents of the oil have been examined by Schimmel & Co.[3]). They were fractionated in vacuum.

Cineol. The lowest boiling fraction (b. p. 40 to 50° under 5 mm. pressure) had a decided odor of cineol. After terpenes and other readily oxidizable substances had been removed by oxidation with 3 p. c. permanganate solution, the residual oil was distilled with steam and the oily distillate subjected to fractional distillation under ordinary pressure. Between 170 and 180° a small amount was collected which, when oxidized with permanganate according to O. Wallach and E. Gildemeister[4]), yielded cineolic acid melting at 202 to 203°. It was further identified by means of its iodol derivative melting at 112°.

l-α-Phellandrene. The next higher fraction ($\alpha_D - 36° 36'$) gave the phellandrene test with nitrous acid (m. p. of nitrite 119 to 120°). Inasmuch as the nitrite was dextrogyrate ([α]$_D$ in 10 p.c. chloroform solution $+ 95°$) the underlying hydrocarbon is *l*-phellandrene.

[1]) Journ. de Pharm. 13 (1827), 466. Comp. also *ibidem* 11 (1825), 187; Trommsdorff's Neues Journ. d. Pharm. 11, I (1825), 127.

[2]) Liebig's Annalen 131 (1864), 277.

[3]) Report of Schimmel & Co. April 1904, 75.

[4]) Liebig's Annalen 246 (1888), 268.

Caryophyllene. Fraction 120 to 125° (6 mm.), when treated according to the Bertram-Walbaum method with sulphuric-acetic acid mixture, supplied a good yield of caryophyllene hydrate, m. p. 97°, which was further characterized by its phenyl urethane melting at 137°. The caryophyllene nitrosate, after recrystallization from benzene, melted at 159°, the nitrolpiperidide at 146 to 147°.

Eugenol methyl ether. The high specific gravity (d_{18} 0.941) of fraction 120 to 125° (6 mm.) suggested the presence of oxygenated constituents in addition to caryophyllene. A Zeisel methoxyl determination gave a positive result. When oxidized with potassium permanganate fraction 248 to 260 yielded veratric acid melting at 179 to 180°, thus establishing the presence of eugenol methyl ether.

Palmitic Acid. The alkali-soluble constituents upon distillation yielded a residue which soon congealed to a crystalline mass. After recrystallization from diluted alcohol, fine needles were obtained that melted at 60° and the analysis of the silver salt of which agreed with palmitic acid.

The presence of small amounts of terpene alcohols is probable, though no chemical proof therefore has yet been brought.

The further investigation covered the assay of a normal self-distilled pimento oil which had the following properties: d_{15} 1.044; α_D — 4 30'. The eugenol content was determined with 3 p.c. sodium hydroxide solution according to the methods of Verley and Boelsing (vol. 1 p. 593). The first method yielded 78 p.c. eugenol, the second method 72.8 and 72.9 p.c. respectively. The methoxyl determination of the non-phenol oil according to Zeisel yielded the following results: 1.527 g. gave 1.9613 g. AgI. Computed for non-phenol oil = 43.6 p.c. methyl eugenol, for the total oil = 9.6 p.c.

504. Oil of Pimento Leaves.

The Imperial Institute of London[1]) reports on an oil distilled in Jamaica from pimento leaves *(Pimenta officinalis,* Lindl., *Myrtaceæ)* which possessed the following properties: d_{15} 1.026; α_D — 5° 30'; soluble in 1.6 vol. of 70 p.c. alcohol. 68 p.c. of the oil consisted of phenols, principally *eugenol.*

[1]) Bull. Imp. Inst. 11 (1913), 438.

505. Oil of Bay.

Oleum Myrciæ. — Bayöl. — Essence de Bay.

Origin. Inasmuch as the numerous species of the genera *Pimenta* and *Myrcia* are variable and resemble each other closely, the minor botanical differences are not always noted while gathering the leaves, hence the commercial bay leaves are not always obtained from one and the same plant, but are mixtures of the leaves of several species[1]). According to E. M. Holmes[2]) the parent plant of the genuine bay leaves is *Pimenta acris,* Wight (*Eugenia acris,* Wight et Arnott) and not *Myrcia acris,* D.C. as stated by other botanists.

The bay tree is indigenous to the West Indies. It thrives particularly in the island of Dominica, which supplies the best bay leaves, also in St. John, Bermuda, Montserrat, Saba, Antigua, Barbadoes and Porto Rico, but not in St. Thomas, the principal island for the production of bay rum.

When the plants are five years old the leaves are picked for the first time, more especially during the dry months February, March and April. A ten year old tree yields annually from 60 to 100 lbs. of leaves, for which the price of 2 cents per pound is paid in St. John.

Experiments made in Montserrat with the cultivation of the bay tree have yielded fairly good results[3]). In 1908, 850 one year old seedlings were planted per acre, at a distance of 6 ft. in the row, the rows 9 ft. apart. Between the rows cotton was planted. The first leaf harvest was conducted in 1911 when the shrubs were 6 ft. high. In another part of the island the yield from an experimental plot amounted to 2660 lbs. per acre in 1905 and 8844 lbs. in 1910, thus showing that the yield increases rapidly.

In the Cameroons also the bay tree flourishes. An oil sent for trial to Schimmel & Co.[4]) by the Botanical Garden in Victoria was fully the equivalent of the West Indian oil. (Comp. Properties.)

[1]) J. C. Sawer, Odorographia. London 1894, vol. II. p. 56.

[2]) Pharmaceutical Journ. III. 21 (1891), 837.

[3]) Report of the Botanic Station, Montserrat 1910 to 1911, p. 16; Bull. Imp. Inst. 10 (1912), 147.

[4]) Report of Schimmel & Co. October 1903, 13.

In addition to the genuine bay tree there occurs in most of the West Indies enumerated, also in Tortula and Trinidad[1]) a variety *Pimenta acris* var. *citrifolia* (*Myrcia pimentoides*, D.C.; *Pimenta citrifolia,* Kosteletzky) which is known as *Lemoncilla* (*Bois d'Inde citron* or "false bay") because of the lemon-like odor of its leaves, which are therefore also known as citronella leaves. The oil obtained from these leaves is rich in citral, hence cannot be used as bay oil.

As adulterant of bay leaves those of *Myrcia coriacea*, D.C. have been observed. Moreover, the leaves of *Canella alba*, known in Antigua as "false" or "bastard cinnamon" are at times mistaken for bay leaves[2]).

Production. Although, as already mentioned, the bay tree does not grow in St. Thomas, this island is nevertheless the principal place of production of bay oil and bay rum. The leaves used for distillation are imported principally from Porto Rico, St. John and Dominica. Not only are the leaves, but the young shoots as well used for the purpose of distillation. They are distilled in copper stills of about 200 gals. (abt. 900 liters) capacity which will hold about 400 lbs. of green leaves. The still is filled with water and 35 lbs. of common salt are added or one-third of the charge in sea water is used. The oil yield varies with the season, and the locality from which the leaves are obtained. On an average 130 to 140 lbs. of green leaves yield one flask (= $\frac{1}{6}$ gal. = 0.76 liter) of oil, corresponding to a yield of approximately 1.2 to 1.3 p.c.

In the course of the distillation a part of the oil rises to the surface, another part sinks to the bottom. Both portions must be mixed in order to obtain a normal oil. This, however, is not always done properly since not infrequently oils are obtained which are either too light or too dense. The yield of oil from dry leaves fluctuates between 2.5 and 3.5 p.c. The oil from Dominica is regarded as an especially good product.

The quality of the oil made in the Leeward Islands is poor, a fact attributable largely to careless distillation. Frequently the

[1]) Report of Schimmel & Co. October 1896, 73.

[2]) Fr. Watts and H. A. Tempany, West Indian Bulletin 9 (1908), 275; Report of Schimmel & Co. April 1909, 21; October 1909, 28. — W. C. Fishlock, West Indian Bulletin 12 (1912), 513; Report of Schimmel & Co. April 1913, 30.

light and heavy oils are sold separately when it may occur that the light oil is rejected as having been adulterated with petroleum. The yield from 120 to 140 lbs. of green leaves amounts to $26^2/_3$ fl. oz. (1.1 to 1.4 p.c.)

Watts and Tempany[1]) have studied the influence of the age of the bay leaves on the yield of the oil by distilling young and old leaves from Montserrat separately. The results, however, were such that no direct conclusions could be drawn.

Bay rum is prepared by distillation of bay leaves with either rum of a high alcohol percentage or by mixing oil of bay with either rum or alcohol. The bay rum prepared by distillation is the best. For this purpose 65 gals. of Demerara rum are added to 400 lbs. of green leaves or 200 lbs. of dry leaves in a copper still and the apparatus filled with water. The distillate constitutes the genuine bay rum of commerce.

Properties. Oil of bay is a yellowish liquid which, when exposed to the air, soon becomes brown; its odor is pleasant, reminding of that of clove oil; its taste pungent and spicy; d_{15} 0.965 to 0.985, in case of poorer oils as low as 0.951; α_D, lævogyrate, up to $-2°$, rarely up to $-3°$; n_{D20} 1.510 to 1.520; phenol content (eugenol and chavicol) 59 to 66 p.c., in case of poorer oils as low as 40 p.c. (determined with 3 p.c. caustic solution); freshly distilled oil is soluble for the most part in 1 to 2 vol. of 70 p.c. alcohol, however, the solubility decreases rapidly, and frequently the oils give a clear solution with 90 p.c. alcohol only in concentrated form. This behavior is attributed to the polymerization of the myrcene contained in the bay oil.

Properties of oils of special sources.

Source	d_{15}	α_D	n_{D20}	Phenol Content
Cameroons[2]) . .	0.9753	$-3°$	—	64 p.c.
Bermuda[3]) . .	1.0301	$-3°4'$	1.53012	61 ,,
Guadeloupe . .	0.934[4])	$-2°46'$	–	38 ,,
,, . .	0.926[4])	$3°10'$	—	41 ,,
,, . .	0.980[4])	$-1°48'$		,,

[1]) West Indian Bulletin 9 (1908), 273; Report of Schimmel & Co. April 1909, 21.

[2]) Report of Schimmel & Co. October 1908, 13.

[3]) *Ibidem* April 1904, 13.

[4]) *Ibidem* April 1903, 13.

Source	$d_{15°}$	α_D	$n_{D20°}$	Phenol Content
Guadeloupe . .	0.9682	$-1°12'$		35 p.c.
„ . .	0.9474	$-1°20'$	..	24 „
„ . .	0.9627	$-1°50'$	—	43 „
Fiji Islands[1]) . .	0.9893	$-1°$	1.52008	23 „
„	0.9605	$-2°10'$	1.51182	24 „

Lemon bay oil.

					Citral content
Trinidad[2]) . . .	0.882 (25°)	$-0°37'$		— „	65 p.c.
Tortola[3]) . . .	0.8937 ($\frac{27°}{16.8°}$)	$-0.16°$	—	10 „	44 „

Composition. The identity of the heavy constituent of the oil with *eugenol*, appears to have been first recognized by G. T. H. Markoe[4]). The first detailed examination of the oil was made by O. Mittmann[5]). In addition to eugenol he found *methyl eugenol*, the presence of which was later confirmed by others. Upon fractionation he obtained a small portion distilling between 160 and 165° which he supposed to be a mixture of two terpenes. The lower boiling one he regarded as pinene, the higher boiling one as dipentene.

According to a later investigation by F. B. Power and C. Kleber[6]) neither of these two terpenes is contained in bay oil. However, a number of constituents, overlooked by Mittmann, were found. In the lowest boiling fraction (67 to 68° under 20 mm pressure) they found a new hydrocarbon, the first representative of the olefinic terpenes which they named *myrcene* (see vol. I. p. 279).

In addition to myrcene, oil of bay contains l-*phellandrene* (nitrite) but no other representative of the terpenes.

The oil freed from phenols and terpenes yielded with sodium bisulphite a solid compound which in turn yielded *citral* (citryl-,ϑ-naphthocinchoninic acid). After removal of the citral an oil remained that had an anise-like odor and which consisted in part

[1]) Report of Schimmel & Co. October 1909, 27.

[2]) *Ibidem* October 1896, 73 and April 1909, 21.

[3]) Watts and Tempany, West Indian Bulletin 9 (1908), 275; Report of Schimmel & Co. April 1909, 21.

[4]) Proc. Am. Pharm. Ass. 25 (1877), 438; Pharmaceutical Journ. III. 8 (1878), 1005.

[5]) Arch. der Pharm. 227 (1889), 529.

[6]) Pharm. Rundsch. (New York) 13 (1895), 60.

of *methylchavicol*. Upon oxidation it yielded anisic acid, and when treated with alcoholic potassa it was converted into anethol. The highest boiling portion of the oil contained methyl eugenol.

Upon treating the phenols, recovered from their alkali derivatives, with methyl iodide, Power and Kleber obtained a mixture of methyl eugenol and methyl chavicol, thus revealing the presence of *chavicol* side by side with that of eugenol in oil of bay.

Arranged quantitatively, oil of bay contains the following constituents: eugenol, myrcene, chavicol, methyleugenol, methylchavicol, phellandrene, citral.

In the aqueous distillate Schimmel & Co.[1]) found *methyl alcohol, furfurol* and *diacetyl*.

Adulteration and Tests. Oils which differ from the normal by a low specific gravity are in many instances products in the bulking of which the correct proportions of light and heavy oils have not been observed. Sometimes, however, they are products adulterated with petroleum[2]).

Inasmuch as oil of bay contains no pinene, adulteration with turpentine oil can be detected without difficulty. From 10 cc. of oil of bay contained in a small fractionating flask, 1 cc. is slowly distilled off. To the distillate 1 cc. of amyl nitrite and 2 cc. of glacial acetic acid are added. To the mixture, kept cold in a freezing mixture, a solution of equal parts of glacial acetic and hydrochloric acids is added drop by drop so long as a blue coloration is produced. In the presence of pinene a precipitation of pinene nitrochloride results. By this method the presence of 10 p.c. turpentine oil in oil of bay can be detected.

506. Oil of Bay Berries.

Upon distillation, bay berries from the Bermudas[3]) yielded 3.66 p.c. of a yellowish-brown oil with an aromatic odor that was distinct from that of ordinary oil of bay. d_{15° 1.0170; α_D —7°3'; phenol content 73 p.c.; soluble in 1.5 vol. of 70 p.c. alcohol, the solution becoming turbid upon the addition of about 4 vol., soluble in 0.5 vol. and more of 80 p.c. alcohol.

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[1]) Report of Schimmel & Co. April 1901, 13.
[2]) *Ibidem* October 1902, 13.
[3]) *Ibidem* April 1905, 85.

The phenols consist of *eugenol* (m.p. of benzoyl compound about 70°). The non-phenol oil is rich in l-*phellandrene* (m.p. of nitrite 103 to 104°). Myrcene does not appear to be present in the oil.

Bay berries from Mauritius, which Schimmel & Co.[1]) had obtained from the Imperial Institute in London, yielded upon distillation 3.3 p.c. of a light brown oil, which, as to odor and other properties, closely resembled those of West Indian oil of bay leaves. $d_{t_{15}°}$ 0.9893; $\alpha_D - 1°20'$; $n_{D_{20}°}$ 1.51902; eugenol content 70 p.c.; soluble in 0.8 vol. and more of 80 p.c. alcohol.

507. Oil of Campomanesia reticulata.

From the fresh leaves of *Campomanesia reticulata*, Berg, (family *Myrtaceæ*) which is indigenous in Brazil, Theo. Peckolt[2]) obtained 0.0029 p.c. of oil upon distillation. It was limpid, possessed a burning, spicy taste and an agreeable myrtle-like odor.

508. Oil of Calyptranthes paniculata.

Labled as "May oil" Schimmel & Co.[3]) obtained from Porto Rico a distillate from *Calyptranthes paniculata*, Ruiz et Pav. (family *Myrtaceæ*). The odor of this oil resembled that of lemongrass; specific gravity 0.9509 at 15°; optical rotation ---1°52'. Whereas the oil was soluble in 80 p.c. alcohol, it was but incompletely soluble in 70 p.c. alcohol. The oil contained 62.5 p.c. citral.

509. Oil of Cloves.

Oleum Caryophyllorum. — Nelkenöl. — Essence de Girofle.

Origin and Production. The clove tree, *Eugenia caryophyllata*, Thunb. (*Caryophyllus aromaticus*, L.) an evergreen belonging to the family *Myrtaceæ* is indigenous to the Philippines and is now cultivated in Amboina, Réunion, Mauritius, Madagascar and Malacca (Penang). On a larger scale, however, it is cultivated in the East African islands Zanzibar[4]) and Pemba, the two producing about seven-eighths of the entire world's output of cloves.

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[1]) Report of Schimmel & Co. October 1910, 21.
[2]) Berichte d. deutsch. pharm. Ges. 13 (1903), 358.
[3]) Report of Schimmel & Co. April 1904, 95.
[4]) Comp. O. Baumann, *Der Sansibar-Archipel. II. Heft, Die Insel Sansibar, III. Heft, Die Insel Pemba.* Leipzig 1897 and 1899. Likewise: A. Engler and

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Cloves consist of the air-dried buds gathered before they are completely developed. The inflorescence is a cyme consisting of as many as 35 individual flowers. Each floret has a fleshy base *(receptaculum)* almost 1 cm. long, which at first is light in color, then becomes green and, shortly before the expansion of the bud, turns dark red. With this change in color the bud is collected and air-dried, because it is then richest in oil. The buds of cultivated trees, all parts of which are aromatic, contain more oil than those of the wild tree.

Formerly the fruits collected just before maturity entered commerce by the name of *anthophylli,* Ger. *Mutternelken.*

For propagation perfectly fresh seeds only are suitable. They should be shipped under water. The seedlings grow very slowly and can be transplanted only after they are 3 or 4 years old. Moreover, they must be carefully protected against the direct rays of the sun. The difficulty in raising the tree has restricted its cultivation. Outside of Zanzibar and Pemba it is but rarely found. Pemba yields three times as many cloves as Zanzibar.

The harvest must be collected in a comparatively short time. During it men, women and children spend the greater part of the day in the trees. The picked cloves are dropped into a cloth tied around the neck. Later the cloves proper are separated from the stems and dried on mats in front of the houses.

As already stated, cloves consist of the unexpanded flower buds which are picked as soon as they develop a delicate purplish-red color. If the picking be delayed too long the bud expands and a small, star-shaped, white flower makes its appearance. After a day or two the white floral leaves drop, the ovary swells and an olive-green fruit develops. This contains a large endocarp and has a purplish, fleshy pericarp, tasting of cloves, which is eaten only by monkeys.

The clove trees are not pruned by the Arabs, hence develop into a dense mass of branches. Inasmuch as the buds develop only in the upper part of the tree, their harvest is rendered very

G. Volkens, *Über den Gewürznelkenbau in Sansibar.* Notizbl. bot. Gart. Berlin. No. 9. (August 1897) . J. E. E. Craster, Pemba, the spice island of Zanzibar. or ticle may be found in the Chemist and Druggist 83 [1913],

difficult and, in part, impossible. It is assumed that rational pruning and fertilizing would increase the yield by fifty per cent.

For distillation purposes only the Zanzibar cloves (which designation includes those from Pemba) are used. The cloves from Amboina and Réunion are richer in oil and, on account of their better appearance, demand a higher price. The difference in oil yield, however, is not equal to the difference in price. The Madagascar cloves from St. Marie, on the north point of the island, demand the highest price. They yield a large percentage of oil, which Paris perfumers regard as finer than other oils, an opinion that is not shared by all[1]).

Cloves are distilled either entire or in comminuted condition. According to the method of distillation (water or dry steam) either a relatively denser oil, richer in eugenol, or a lighter oil richer in non-phenol constituents, is obtained. The oily distillate floats in part on the water, in part sinks. By mixing both parts the normal oil is obtained. The yield from Zanzibar cloves amounts to from 16 to 19 p.c.

Production and Commerce. As already mentioned, cloves and clove stems from East Africa alone come into consideration so far as the volatile oil industry is concerned. Hence the following statistics, taken from the reports of Schimmel & Co., apply to them only.

The following figures record the annual harvest of cloves in East Africa from the year 1893 to 94 to the year 1911 to 12[2]): —

	Zanzibar Frasilas[3])	Pemba Frasilas[3])		Zanzibar Frasilas[3])	Pemba Frasilas[3])
1893/94 . .	197 710	402 621	1903/04 . .	28 369	96 792
1894/95 . .	102 208	307 860	1904/05 . .	79 860	675 683
1895/96 . .	165 901	413 124	1905/06 . .	181 536	109 931
1896/97 . .	84 592	224 362	1906/07 . .	55 833	202 633
1897/98 . .	44 941	150 703	1907/08 . .	213 667	541 998
1898/99 . .	149 417	481 565	1908/09 . .	165 733	449 685
1899/1900 .	59 741	206 640	1909/10 . .	109 682	300 043
1900/01 . .	37 567	201 192	1910/11 . .	51 996	139 307
1901/02 . .	43 626	321 599	1911/12 . .	218 023	590 771
1902/03 . .	175 420	251 780			

[1]) Report of Schimmel & Co. April 1892, 20.

[2]) The harvest year is from August 1st to July 31st.

[3]) 1 Frasila = 35 lbs. Engl. = 15.876 kg.

The annual export of cloves from Zanzibar, from which all East African cloves are shipped, amounted to[1]: —

1898	. .	10 856 566 lbs. Engl. valued at	2 155 956	Rupees
1899	. .	16 593 340 „ „ „ „	2 958 487	„
1900	. .	11 788 095 „ „ „ „	2 372 227	„
1901	. .	11 962 069 „ „ „ „	2 465 373	„
1902	. .	10 125 769 „ „ „ „	2 957 589	„
1903	. .	12 092 138 „ „ „ „	2 795 980	„
1904	. .	14 502 775 „ „ „ „	4 986 449	„
1905	. .	15 312 952 „ „ „ „	4 306 090	„
1906	. .	15 105 760 „ „ „ „	5 349 545	„
1907	.	18 214 668 „ „ „ „	5 941 817	„
1908	. .	14 974 872 „ „ „ „	3 974 398	„
1909	. .	20 285 001 „ „ „ „	4 956 142	„
1910	. .	12 783 149 „ „ „ „	3 802 048	„

Table of exports to individual countries and ports[2]: —

	1898 lbs.	1898 Rup.	1899 lbs.	1899 Rup.	1900 lbs.	1900 Rup.
Europe . . .	4 138 086	797 375	8 028 780	1 394 217	5 235 380	1 031 952
Rotterdam .	—		4 473 240	786 212	2 674 160	537 810
Amsterdam	...	.	294 000	49 395	84 000	18 000
London . .	.	—	1 432 475	254 852	1 404 968	274 520
Hamburg .	—		1 249 850	204 267	715 260	122 912
Marseilles .	—	---	292 215	52 229	217 000	49 800
America . .	729 960	149 402	648 970	110 008	719 600	150 079
Asia . .	5 912 800	1 194 032	7 599 517	1 397 837	5 769 233	1 177 754
Africa . .	75 720	15 147	316 073	56 425	63 814	12 442

	1901 lbs.	1901 Rup.	1902 lbs.	1902 Rup.	1903 lbs.	1903 Rup.
Europe . . .	4 470 632	888 110	4 160 485	852 006	3 551 966	765 411
Rotterdam .	2 330 764	466 168	2 210 420	472 430	677 618	—
London . .	1 841 493	364 955	1 295 910	253 490	2 014 289	—
Hamburg .	125 720	23 220	425 015	78 172	465 995	—
Marseilles .	133 000	25 200	188 475	39 214	251 664	---
America . .	252 000	50 700	412 300	88 031	852 361	189 102
Asia	7 081 471	1 496 053	5 412 143	1 091 456	7 560 852	1 812 787
India (Bombay)	--	—	4 924 255	996 820	—	—
Africa . . .	153 996	30 510	140 841	26 096	126 959	28 680

[1] The export of cloves amounts to about 35 to 40 p. c. of the total export.

[2] Since the bills of lading are for optional transhipment to Rotterdam, London or Hamburg, the actual amounts may not agree with the declared amounts. So far as Germany is concerned, it should be noted that not all of its imports come via Hamburg. Many firms make their purchases in Holland and have them delivered by rail.

	1904	1904	1905	1905	1906	1906
	lbs.	Rup.	lbs.	Rup.	lbs.	Rup.
Europe . . .	7 312 375	2 633 787	5 673 319	1 676 468	8 939 789	3 176 924
Rotterdam .	1 096 860	– ·	1 814 460	554 887	1 543 310	557 320
London . .	4 779 340	—	2 762 850	820 638	2 650 919	915 629
Hamburg .	444 995	—	633 284	181 335	3 841 300	1 387 202
Marseilles .	251 669	...	218 750	54 230	585 760	207 338
America . .	2 056 175	713 420	1 769 860	401 027	717 900	238 975
Asia . . .	4 839 524	1 601 061	7 810 508	2 123 255	5 355 875	1 901 368
India . . .	—	1 554 191		1 985 878	—	1 782 609
Africa . . .	94 701	38 191	59 265	15 340	92 196	32 278

	1907	1907	1908	1908	1909	1909
	lbs.	Rup.	lbs.	Rup	lbs.	Rup.
Europe . . .	10 457 830	3 387 448	7 197 375	1 894 363	10 638 889	2 596 530
Rotterdam .	952 006	295 300	560 351	141 704	3 007 720	712 148
London . .	3 298 930	1 112 693	2 283 330	600 075	1 592 492	405 447
Hamburg .	5 529 056	1 770 961	3 296 968	886 785	4 498 151	1 111 183
Marseilles .	418 850	125 867	894 986	225 757	1 041 827	250 876
America . .	1 102 420	306 061	651 780	184 578	2 364 940	589 941
Asia . . .	6 553 453	2 215 262	7 051 342	1 876 332	7 183 252	1 746 728
India .	· ·	2 149 154	—	—	—	—
Africa . . .	100 965	33 046	74 375	18 725	97 920	22 843

	1910	1910	1911	1912
	lbs.	Rup.	Rup.	Rup.
Europe . . .	4 800 676	1 323 287	2 411 944	1 943 107
Rotterdam .	1 685 900	432 485	—	—
London . .	565 829	215 019	811 758	602 838
Hamburg .	2 177 370	560 317	1 267 586	1 153 547
Marseilles .	188 467	59 251	—	—
America . .	1 096 215	303 592	1 050 971	570 952
Asia . . .	6 788 231	2 138 243	3 030 477	2 594 377
Africa . . .	128 019	36 926	– ·	.—

The preceding figures taken from the Report of the German Consulate at Zanzibar, are, herewith, supplemented by data from the British Consulate.

	1904	1905	1906	1906	1907	1907
	£ Sterl.	£ Sterl.	Cwt.	£ Sterl.	Cwt.	£ Sterl.
Total export . .	:—	287 073	134 882	356 836	162 631	396 121
Great Britain . .	119 913	54 709	23 667	62 042	26 455	74 179
British India . .	98 454	132 236	44 610	112 162	56 542	134 071
Netherlands . . .	24 866	36 992	13 801	37 155	8 500	19 687
United States . .	47 651	32 735	6 410	15 932	9 843	20 404
German Empire .	9 221	12 089	34 297	92 840	49 367	118 064
France	16 274	3 615	5 230	13 822	3 741	8 391
Austria-Hungary .	3 944	· 2 573	1 344	3 522	625	1 405
Italy	..	—	1 469	3 685	1 688	4 103
Other countries .	· ·	—	4 054	9 798 ·	2 870	6 811

	1908 Cwt.	1908 £ Sterl.	1909 Cwt.	1909 £ Sterl.	1910 Cwt.	1910 £ Sterl.
Total export . .	133 704	264 960	181 116	330 410	114 135	253 470
Great Britain . .	20 389	40 005	16 004	27 030	5 052	14 335
British India . .	61 312	121 944	62 329	113 314	59 106	139 946
Netherlands . . .	5 003	9 447	26 826	47 475	15 053	28 828
United States . .	5 841	12 305	21 115	39 330	9 787	20 240
German Empire .	29 438	59 119	40 162	74 079	19 440	37 354
France	8 205	15 150	9 302	16 725	1 683	3 950
Austria-Hungary .	759	1 456	2 054	3 557	629	1 415
Italia	538	926	2 049	3 591	1 005	2 337
Other countries .	2 219	4 708	1 275	5 309	2 380	5 065

	1911 Cwt.	1911 £ Sterl.	1912 Cwt.	1912 £ Sterl.
Total export . . .	180 905	436 991	136 178	342 173
Great Britain . .	23 939	54 117	16 361	40 189
British India . . .	76 070	198 239	56 735	168 935
Netherlands . . .	938	1 975	—	—
United States . .	31 436	70 065	23 005	38 063
German Empire .	36 014	84 506	32 104	76 903
France	3 069	7 026	1 845	4 324
Austria-Hungary .	2 453	5 401	2 048	4 250
Italy	2 813	6 076	1 156	2 394
Other countries .	4 173	9 586	2 924	7 115

Table of cloves imported into Germany via Hamburg.

1898	1899	1900	1901	1902	1903
13 000	24 500	27 000	19 300	—	17 000 bales

1904	1905	1906	1907	(1908/13 wanting)
9 600	19 500	24 000	29 600 bales.	

According to the Hamburg Committee on Commerce and Shipping the following amounts of cloves were imported *via* the sea[1]).

1908	. . . .	23 202 dz.	valued at	2 367 530 ℳ
1909	. . . .	27 514 „	„	„ 2 479 380 „
1910	. . . .	20 298 „	„	„ 1 934 350 „
1911	. . . .	21 269 „	„	„ 2 544 600 „
1912	. . . .	21 964 „	„	„ 2 400 020 „
1913	. . . .	21 109 „	„	„ 2 990 600 „

[1] Private communication.

Clove stems.

Concerning the production of clove stems but meagre data are available. The harvest of 1911 was valued at 193535 rupees, that of 1912 at 376775 rupees. Almost the entire harvest is exported to Europe, more particularly to Hamburg. The detailed figures, according to communications of the German Consulate at Zanzibar, are herewith tabulated.

	1898 lbs.	1898 Rup.	1899 lbs.	1899 Rup.	1900 lbs.	1900 Rup.
Europe . . .	584640	24055	3605245	104351	1743426	70453
Asia	305561	14845	216483	6748	220447	11621
America . . .	336875	19657	555940	31708	98000	7700
Africa . . .	—	—	—	—	-	.-

	1901 lbs.	1901 Rup.	1902 lbs.	1902 Rup.	1903 lbs.
Europe . . .	1290868	66556	2158642	106927	1738468
Asia	210140	13350	177252	9965	197321
America . . .	140000	106000	—	—	678178
Africa . . .	—	---	.	.	—

	1904 lbs.	1904 Rup.	1905 lbs.	1905 Rup.	1906 lbs.	1906 Rup.
Europe . . .	1001666	96536	3777062	285818	2317305	222607 [1]
Asia	145845	12671	63835	3622	63056	6831
America . . .	87655	10003	149426	9680	--	-
Africa . . .	—	—	-		2065	285

	1907 lbs	1907 Rup.	1908 lbs.	1908 Rup.	1909 lbs.	1909 Rup.
Europe . . .	2055415	190197 [1]	2361964	172398	4318057	278905
Asia	48125	4708	34787	2418	42035	3024
America . . .	179900	15060	552160	39972	186620	12669
Africa . . .	—	—	—	—	—	—

	1910 lbs.	1910 Rup	1911 Rup.	1912 Rup.
Europe . . .	2262293	182386	191911	374951
London . .	—	—	34184	128059
Hamburg .	—	—	147113	237688
Asia	42665	3367	1112	1824
America . .	—	—	—	—
Africa . . .	—	—	—	—

[1]) To Hamburg: 1906 213618 Rup., 1907 175648 Rup.

˙ To the several European ports the following amounts (in
lbs. Eng.) were shipped: —

	1898	1899	1900	1901	1902
Hamburg . . .	456 890	2 980 110	1 478 226	1 212 668	1 873 874
London	74 900	370 335	83 160	33 700	46 200
Marseilles . . .	38 850	179 900	28 000	31 500	27 300
Rotterdam . . .		. .	- -	112 000	—
Amsterdam . . .		-	42 000	42 000	201 095

The imports (in dz.) of clove stems into Hamburg amounted
to: ---

1897	1898	1899	1900	1901	1902
1500	3420	9330	7305	4160	---

1904	1905	1906	1907	1908	1909
3330	12 300	8500	12 000	7675	13 000

According to statistics by the Hamburg Committee on
Commerce and Shipping the imports, by water, of clove stems
at Hamburg were [1]): —

1908 . . . . . 12 064 dz. valued at 396 500 ℳ
1909 . . . . . 20 552 ,,   ,,   ,, 545 830 ,,
1910 . . . . . 10 110 ,,   ,,   ,, 307 440 ,,
1911 . . .˙. . 8 391 ,,   ,,   ,, 361 390 ,,
1912 . . . . . 19 756 ,,   ,,   ,, 727 610 ,,
1913 . . . . . 7 336 ,,   ,,   ,, 409 210 ,,

The Government of Zanzibar possesses plantations covering
an area of 17 000 acres.

The plantations of Madagascar comprise 400 000 trees of
which 230 000 are on the island of St. Marie. They cover an
area of 2.391 acres, of which 415 acres have been planted by
Europeans. The export (almost exclusively to France) in 1911
amounted to 288 237 lbs. with a value of 10 000 £ [2]). According
to another statement, the exports in 1911 amounted to 128 tons
and in 1912 to 207 tons [3]).

According to A. Chevalier [4]) the clove tree is today fairly
widely distributed in the French Congo, although a clove culture

[1]) Private communication.
[2]) Pharmaceutical Journ. 89 (1912), 571.
[3]) Report of Schimmel & Co. October 1913, 46.
[4]) Compt. rend. 155 (1912), 1091.

Map
of the
Clove Districts
of
ZANZIBAR and PEMBA.
Scale 1:800 000

Clove districts
Cloves areas, map title
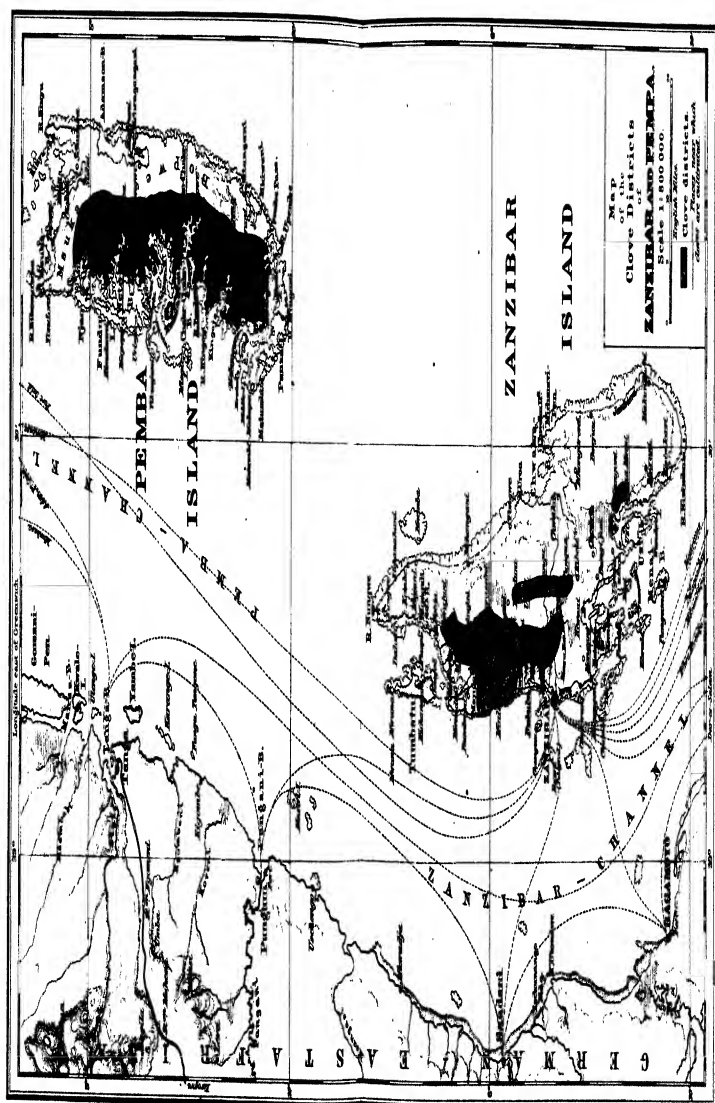
cannot be regarded as existing. About 25 years ago the tree was completely unknown. In 1887 the first plantings were made. In 1893 the trees blossomed for the first time. A ten year old tree in the French Congo yields from 5 to 10 kg. of cloves.
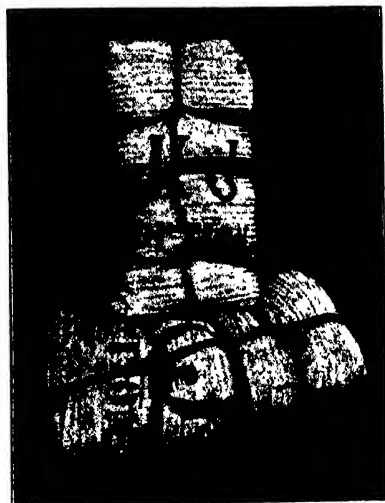
Fig. 17. Clove bales (Gonjes).

Properties. According as to whether the cloves are distilled whole or in comminuted condition, oils of differing properties are obtained. Whole cloves yield an oil with high eugenol content and a density of more than 1.06; comminuted cloves an oil with lower eugenol content and a density below 1.06. When freshly distilled, clove oil is an almost colorless or but yellowish liquid, of highly refractive capacity, which becomes darker with age. Its odor is sharp and spicy, the taste persistently burning. $d_{15°}$ 1.043 to 1.068; a_D up to $-1°35'$; $n_{D20°}$ 1.530 to 1.535; soluble (sometimes with slight turbidity) in 1 to 2 vol. and more of 70 p.c. alcohol. Only fresh, socalled extra light oils, are soluble in 2.5 to 3 vol. of 60 p.c. alcohol, the solution not infrequently becoming turbid upon dilution, only very high percentage oils yield solutions that remain clear. Eugenol content (determined with 3 p.c. hot soda solution; comp. vol. I, p. 591) 78 to 95 p.c.,

very rarely up to 98 p.c. According to this assay the acet-
eugenol present is determined as eugenol.

Properties of Special Oils.

Origin	Yield of oil[1]	$d_{15°}$	a_D	Eugenol content
Amboina[2] . .	19 p.c.	1.0465	— 1° 4'	79 p.c.
Seychelles[3] . .	19.3 „	1.0470	— 1° 30'	85 „
„ [3] . .	19.8 „	1.0485	— 1° 6'	86 „
Ceylon	21 „	1.0456	— 2° 30'	87 „
„	21.3 „	1.0477	— 2°	85 „
Mauritius[4] . .	18.1 „	1.0514	- - 0° 23'	89.1 „
„ [5] . .	—	1.0614	— 0° 24'	93 „
„ [5] . .	—	1.0681	— 0° 20'	96. „
Amani[6] . . .	16.6 „	1.0558	- 1° 4'	92 „

Composition. Of the constituents of clove oil, eugenol, which
is present in the free condition to the extent of 70 to 85 p.c.
at first attracted the attention of chemists. (Comp. History,
vol. I, p. 161.)

Eugenol is the most characteristic and valuable constituent
of clove oil. In addition to free eugenol, clove oil contains
aceteugenol; according to E. Erdmann[7]) 2 to 3 p.c., according
to E. C. Spurge[8]) as much as 7 to 17 p.c. This ester is found
in the non-phenol portion of the oil after treatment with diluted
cold alkali. From it the aceteugenol can be removed by
saponification with alcoholic potassa or concentrated aqueous
potassa.

As was already shown by A. H. Church[9]), the oil remaining
after the removal of aceteugenol consists largely of a sesqui-
terpene. This was more thoroughly examined by O. Wallach[10])

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[1]) On distillation of comminuted cloves.
[2]) Report of Schimmel & Co. October 1904, 22.
[3]) *Ibidem* April 1912, 57.
[4]) Bull. Imp. Inst. 8 (1910), 3.—Report of Schimmel & Co. October 1910, 40.
[5]) Report of Schimmel & Co. April 1914, 47.
[6]) *Ibidem* April 1912, 57.
[7]) Journ. f. prakt. Chem. II. 56 (1897), 143.
[8]) Pharmaceutical Journ. 70 (1903), 701, 757.
[9]) Journ. Chem. Soc. 28 (1875), 113; Chem. Zentralbl. 1875, 215.
[10]) Liebig's Annalen 271 (1892), 287.

and designated caryophyllene by him. For properties and deri-
vatives see vol. I, p. 331[1]).

Caryophyllene occurs in clove oil in two modifications; the
lower boiling portion of the sesquiterpene fraction consists for
the most part of *ß-caryophyllene*, which is characterized by its
blue nitrosite melting at 164 to 165˙. Inactive *α-caryophyllene*
boils somewhat higher (m. p. of nitrosochloride 177°) and is
present in smaller amount.

In the highest boiling portions there appears to be another
strongly lævogyrate hydrocarbon which has not yet been further
examined[2]).

The occurrence of small amounts of *salicylic acid* was
pointed out by H. Schenck[3]). The correctness of this state-
ment, however, was questioned by M. Wassermann[4]). Definite
proof of its presence was supplied by E. Erdmann[5]) who sup-
posed that it occurred as the acetosalicylic ester of eugenol.
However, this supposition has not been verified, and H. Masson[6])
showed that is was present as methyl ester.

A number of minor constituents have been found by
Schimmel & Co. in clove oil. Of these the *methyl*-n-*amyl ketone*
(oxidation to valeric and acetic acids; m. p. of semicarbazone
122 to 123°)[7]) is the most important. Although it is present
only to the extent of a fraction of one per cent, it nevertheless
exerts a noteworthy influence on the odor of the oil, being the
bearer of the peculiar fruit-like by-odor.

In addition to this ketone the lowest boiling portions contain
methyl alcohol (m. p. of oxalate 54°)[8]) and *furfurol* (m. p. of

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[1]) Concerning more recent literature on caryophyllene not mentioned
in vol. I, see Report of Schimmel & Co. October 1910, 180. — C. W. Haarmann,
Berl. Berichte 43 (1910), 1505. — E. Deussen, Liebig's Annalen 374 (1910), 111;
388 (1912), 136. — F. W. Semmler and E. W. Mayer, Berl. Berichte 43 (1910),
3451; 45 (1912), 1393.

[2]) C. Vielitz, *Beiträge zur Kenntnis des Caryophyllens aus Nelken-
blütenöl.* Inaug.-Dissert., Leipzig 1912, 14.

[3]) Liebig's Annalen 125 (1863), 14.

[4]) Liebig's Annalen 179 (1875), 369.

[5]) *Loc. cit.*

[6]) Compt. rend. 149 (1909), 795.

[7]) Report of Schimmel & Co. April 1897, 45; April 1902, 24.

[8]) *Ibidem* October 1896, 27.

phenylhydrazone 96°)[1]) to the presence of which the darkening
of the oil may, in part, be attributed. A fraction consisting
apparently of a terpene gave a negative test for α-pinene[2])
Possibly it contains *β-pinene* which was unknown at that time
Like salicylic acid, *benzoic acid* is present as methyl ester[3])[2])
Admixed with the esters, *methyl heptyl ketone* (m.p. of semi-
carbazone 118 to 119°)[4]) was identified but could not be separated
by fractionation.

Valeric aldehyde[5]) may be regarded as a probable con-
stituent. When the lower fractions of the oil were shaken with
acid sulphite solution and the compound thus removed regenerated,
the characteristic odor of this aldehyde with its tendency to
produce coughing, was developed.

A number of new constituents have been described by
H. Masson[5]). By treating fraction 50 to 75° (15 mm.) with
phthalic acid anhydride, he obtained a mixture of alcohols,
of which he identified *methyl-n-amylcarbinol* (heptanol-2)
$CH_3CH(OH)(CH_2)_4CH_3$ (b.p. 157 to 158°; $d_{0°}$ 0.8344) and *furfuryl
alcohol* (b.p. 170 to 171°; $d_{0°}$ 1.1615; m.p. of phenyl urethane
97.5°). The methyl-n-amyl carbinol was further characterized
by its oxidation to methyl-n-amyl ketone (b.p. 151 to 152°). In
fraction 75 to 100° (15 mm.) Masson found *methyl-n-heptyl
carbinol* (nonanol-2), $CH_3CH(OH)(CH_2)_6CH_3$ (b.p. 195 to 196°;
$d_{0°}$ 0.8399) and *benzyl alcohol* (b.p. 206°; $d_{0°}$ 1.0627) which
were identified by their oxidation to methyl-n-heptyl ketone and
benzoic acid respectively. He also revealed the presence of an
unsaturated alcohol (methyl furfuryl alcohol?). The fractions
coming over between 65 and 95° (15 mm.) contained, besides
methyl-n-heptyl ketone, α-methyl furfurol; b.p. 184 to 186°
(ordinary pressure), 75° (20 mm.); $d_{0°}$ 1.1365. It was characterized
by its semicarbazone (m.p. 210 to 211°), its phenylhydrazone
(m.p. 147 to 148°) and by its oxidation to α-methylpyromucic
acid (m.p. 107 to 108°). In fraction 105 to 120° (15 mm.) there
occurs a *dimethyl furfurol* (b.p. 206 to 208°) which, upon

[1]) Report of Schimmel & Co. October 1896, 27.
[2]) *Ibidem* April 1908, 25.
[3]) *Ibidem* April 1902, 24.
[4]) *Ibidem* April 1908, 26.
[5]) Compt. rend. 149 (1909), 630, 795.

oxidation, yields a pyromucic acid melting at 129 to 130°. The position of the methyl groups could not be determined.

Another substance which had previously been found in the oil, *viz. vanillin*[1]), may be assumed to have resulted by atmospheric oxidation of eugenol. It is noteworthy that the vanillin is already contained in the cloves.

Tests. The best means of determining the value of clove oil is to assay its eugenol content, which has been described with sufficient detail in vol. I, pp. 591, 592, 593 and 596 to 598. The simplest method, which suffices for practical purposes, consists in shaking the oil with 3 p. c. soda solution in a cassia flask. However, care should be taken to heat the oil-soda mixture. in a water bath for 10 minutes with repeated shaking so as to make sure of the saponification of the aceteugenol. This assay yields the total eugenol content, *viz.* of free eugenol and its acetyl derivative.

Although this simple method, which enables the recognition of most adulterants is available, grossly adulterated oils have been found in the market. Adulteration with 60 p. c. gurjun-balsam oil[2]), with camphor oil[3]), and with castor oil[4]), have been observed. More common, however, than direct adulteration is the substitution of the cheaper and less fragrant clove stem oil, the detection of which is possible only by a trained sense of smell. Possibly the fact that oil of cloves, but not the oil of clove stems contains aceteugenol may be utilized to differentiate the two oils.

510. Oil of Clove Stems.

Oleum Caryophyllorum e stipitibus. — Nelkenstielöl. — Essence de Tiges de Girofle.

Origin and Production. Clove stems, the flower stems of the cloves, are much less aromatic than the latter and, upon distillation, yield only from 5 to 10 p. c. of oil.

As stated in vol. I, p. 163, oil of clove stems was distilled as early as the middle of the 16th century. During the early

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[1]) A. Jorissen and E. Hairs, Revue intern. scient. popul. falsific. denrées aliment. 4 (1890), 32; Chem. Zentralbl. 1890, II. 828.

[2]) Report of Schimmel & Co. October 1906, 27.

[3]) *Ibidem* April 1910, 43.

[4]) *Ibidem* October 1912, 48.

twenties of the past century, clove stems were distilled with
cloves as a means of cheapening the production of the oil[1]).

Properties. In its properties oil of clove stems closely
resembles that of oil of cloves. Its odor, however, is less
agreeable, hence the oil is not used in high-class perfumery
neither in pharmacy.

According as to whether the stems are comminuted or
not, a lighter or a heavier oil is obtained as with the cloves;
d_{16} 1.040 to 1.067; α_{D} up to $-1°30'$; n_{D20} 1.531 to 1.538; soluble
in 1 to 2 vol. and more of 70 p.c. alcohol; frequently the oils
are soluble in 2.5 to 3 vol. of 60 p.c. alcohol, but upon further
dilution the solution may become opalescent and even turbid,
more particularly those of older oils. Eugenol content (deter-
mined with 3 p.c. soda solution) 85 to 95 p.c., rarely higher.

A clove stem oil obtained from the Seychelles had the
following properties; d_{16} 1.0685; $\alpha_{D} - 0°17'$; eugenol content
almost 100 p.c.; soluble in 2 vol. and more of 60 p.c. alcohol.

Composition. The amount of free eugenol in oil of clove
stems is, as a rule, somewhat higher than in clove oil. The
fact that oil of clove stems having the same density as oil of
cloves yield, according to the benzoyl chloride method, a higher
eugenol content[2]) than corresponding clove oils, is explained by
the absence of the relatively more dense aceteugenol in the
clove stem oils[3]).

Caryophyllene, both *α-* and *β*-caryophyllene, also *methyl-
alcohol* and *furfurol* have been identified in clove stem oil[4]).
Judging by the odor, methyl amyl ketone is likewise present in
clove stem oil though in much smaller amount.

Several substances which seem to be wanting in clove oil,
have been identified in clove stem oil, *viz. naphthalene*[5]) and a
sesquiterpene alcohol $C_{15}H_{26}O$. For the latter F. W. Semmler
and E. W. Mayer[6]) determined the following properties: b. p.

[1]) Martius, Buchner's Repert. f. d. Pharm. 26, II (1827), 278.

[2]) H. Thoms, Berichte d. deutsch. pharm. Ges. 1 (1891), 286.

[3]) E. Erdmann, Journ. f. prakt. Chem. II. 56 (1897), 143.

[4]) For references to the literature on these compounds, see under Oil
of Cloves.

[5]) H. von Soden and W. Rojahn, Pharm. Ztg. 47 (1902), 779.

[6]) Berl. Berichte 45 (1912), 1392.

138 to 148° (8 mm.); $d_{20°}$ 0.9681; α_D — 17; n_D 1.5010; mol. refr. found 68.18, computed for $C_{15}H_{26}O/$ 68.07. Judging from these data the sesquiterpene alcohol in question is bicyclic with one double bond. Its chloride (b. p. 147 to 155° under 12 mm. pressure: $d_{20°}$ 0.990), when treated with alcoholic potassa yielded a hydrocarbon of the following properties: b. p. 123 to 126° (10 mm.); $d_{20°}$ 0.9273; $\alpha_{D20°}$ — 23°; $n_{D20°}$ 1.5024.

From the vacuum distillation residue of the non-phenol oil, freed of its sesquiterpenes, E. Deussen[1]) isolated about 0.1 p.c. of an amorphous substance which was insoluble in alcohol, revealed a rather indefinite melting point at 146°. To it the formula $(C_{21}H_{30}O)_5$ was assigned.

511. Oil of Clove Leaves.

Upon distillation dry clove leaves yield about 4.5 p.c. of oil which resembles clove oil in its properties.

A clove leaf oil from Zanzibar was examined by the Imperial Institute[2]) in London. It had the following properties: $d_{15°}$ 1.0652; soluble in 1.1 vol. and more of 70 p.c. alcohol; eugenol content 85.7 p.c.

For clove leaf oil, said to have come from the Seychelles, the following constants have been reported[3]): $d_{15°}$ 1.0489; α_D — 1°35'; eugenol content 87 p.c.; soluble in 1 vol. and more of 70 p.c. alcohol.

In the laboratory of Schimmel & Co.[4]) six other Seychelles leaf oils have been examined: $d_{15°}$ 1.0324 to 1.0493; α_D — 1°40' to — 1°53'; n_{D20} 1.53329 (1 determination); eugenol content 78 to 87 p.c.; soluble in 1.5 vol. and more of 70 p.c. alcohol; mostly becoming turbid after the addition of 2.5 vol. and more of solvent.

The leaf oils from Mauritius revealed the following properties: $d_{15°}$ 1.061 to 1.067; α_D — 0°50' to — 1°; $n_{D20°}$ 1.5363 to 1.5391; eugenol content 92 to 93 p.c.; clear solution with 1 vol. and more of 70 p.c. alcohol[4]).

[1]) Berl. Berichte 42 (1909), 380, 680.

[2]) Bull. Imp. Inst. 11 (1913), 438.

[3]) *Ibidem* 6 (1908), 111. Comp. also Report of Schimmel & Co. October 1907, 37 and October 1908, 48.

[4]) Report of Schimmel & Co. April 1914, 47.

512. Oil of Anthophylli.

As has been stated on p. 196, the berry-like fruits of the clove tree, collected just before maturity, are known as *anthophylli*, Ger. *Mutternelken*. In an experimental distillation, Schimmel & Co. obtained 2.03 p.c. of a brownish oil with an odor of cloves, but fainter. The following constants were determined: $d_{15°}$ 1.0933; α_D — 3°11'; $n_{D20°}$ 1.54332; phenol content (determined with 3 p.c. soda solution) 88 p.c.; soluble in 1.8 vol. and more of 70 p.c. alcohol. Noteworthy is the unusually high specific gravity, for it exceeds even that of eugenol ($d_{15°}$ 1.071 to 1.074). This difference was emphasized even more in the specific gravity of the isolated phenols, 1.1210 at 15°. The explanation is found in the fact that only about 60 p.c. of the phenols consist of eugenol, the remaining portion consisting of a solid substance. Computed for the original oil, the latter amounts to about 35 p.c., the eugenol content about 53 p.c.

The solid phenol has a faint paraffin-like odor and is well-nigh insoluble in water, but more or less soluble in the common organic solvents, also in aqueous alkali. From alcohol it crystallizes in handsome, thick crystals melting at 44 to 45.5°. It boils between 309 and 310° (754 mm.) and 146 to 149° (4 mm.). It is optically inactive. In the superfused condition its density is 1.188 at 15°. With benzoyl chloride it reacts energetically. Recrystallized several times from alcohol the benzoate melts at 87 to 88°.

513. Cheken Leaf Oil.

The leaves of *Eugenia Cheken* (Molina) Hook. et Arn. (*Myrtus Cheken*, Spr., family *Myrtaceæ*) which are indigenous to Chili and which have repeatedly been recommended for medicinal purposes, contain about 1 p.c. of an oil[1]) which closely resembles the ordinary oil of myrtle.

It is limpid, of yellowish-green color and has a pleasant odor reminding of eucalyptus and sage. $d_{15°}$ 0.8795; α_D + 23.5°. The bulk of the oil, about 75 p.c., boils between 155 to 157°; d 0.8635; α_D + 31.28°, has the composition $C_{10}H_{16}$ and

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[1]) Weiss, Arch. der Pharm. **226** (1888), 666.

with hydrogen chloride yields a monohydrochloride melting at 120°. Heated to 260 to 270° it was changed to dipentene (m. p. of tetrabromide 125 to 126°[1]). From this it becomes apparent that the hydrocarbon boiling between 155 and 157° is d-α-*pinene*.

The fraction boiling about 176° is *cineol* (15 p.c.) as shown by the red crystals of cineol dibromide, $C_{10}H_{18}OBr_2$, formed when bromine is added to the petroleum ether solution.

About 10 p.c. of the oil passes over between 220 and 280°. The composition of this fraction has not yet been determined.

514. Oil of Eugenia Jambolana.

From the seeds of *Eugenia Jambolana*, Lam., a myrtaceous plant of the East Indies, known as Jambul seeds, F. B. Power and T. Callan[1]) isolated 0.05 p.c. of a volatile oil with the following properties: $d_{20°}^{20°}$ 0,9258; α_D — 5°42'. Its color is light yellow and the odor pleasant. The boiling temperature lies between 145 and 155° (25 mm.).

515. Oil of Eugenia apiculata.

A Chilean drug known as *Arrayan* is very popular as a remedy against diarrhœa and lung troubles. According to O. Tunmann[2]) it consists of the young leaves of a small tree, *Eugenia apiculata*, D.C., family *Myrtaceæ*, which are about 15 mm. long and 10 mm. wide. In addition to a tannin-yielding glucoside it contains a volatile oil to which its medicinal virtues are attributed. Schimmel & Co.[3]) worked up a lot of these leaves and obtained 1.27 p.c. of an oil of a brownish color, the odor of which reminded of myrtle, and with the following constants: $d_{15°}$ 0,8920; α_D + 12°40'; $n_{D20°}$ 1.47821; A.V. 5,5; E.V. 25,8; E.V. after acetylation 65,3; soluble in 0.5 vol. and more of 90 p.c. alcohol, from the diluted solution of which paraffin separated; in 10 vol. of 80 p.c. alcohol the oil is not soluble.

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[1]) Pharmaceutical Journ. 88 (1912), 414.

[2]) Pharm. Zentralh. 50 (1909), 887.

[3]) Report of Schimmel & Co. October 1910, 145.

516. Oil of Eugenia occlusa.

As "salam oil" [1]) there was sent to Schimmel & Co.[2]) a sample of oil which had been distilled, with a yield of about 0.05 p.c., from the leaves of *Eugenia occlusa*, Kurz *(Syzygium occlusum,* Miq., family *Myrtaceæ)*. This plant is esteemed as a spice by the Javanese. At about $+ 12^\circ$ the dark-brown oil separates crystals (paraffin?). In addition to other aldehydes it contains not inappreciable amounts of *citral*. The recrystallized semicarbazone melted at 135°. The oil possessed the following constants: d_{15° 0.9567; $\alpha_D - 1^\circ 40'$; n_{D20° 1.48614; soluble in 0.5 vol. and more of 90 p.c. alcohol.

517. Oil of Eugenia uniflora.

According to Th. Peckolt[3]) the seeds of *Eugenia uniflora*, L. *(Stenocalyx Michelii,* Berg, family *Myrtaceæ)*, known in Brazil as *Pitanga amarella*, yield 0.043 p.c. of a yellowish volatile oil possessing an aromatic, pepper-like odor and taste. From the leaves 0.140 p.c. of oil, specific gravity d_{15° 0.963, were obtained.

518. Oil of Backhousia citriodora.

Origin. *Backhousia citriodora*, F. v. M., a tree of the family *Myrtaceæ*, is an Australian tree that is found exclusively between Brisbane and Gympy (Queensland) and which is in danger of extinction because this coastal region is being deforested more and more for other purposes[4]). Inasmuch as the oil yield is but small (about 0.7 p.c.)[5]), the expectation that this oil might serve as a source for citral will scarcely be realized[6]).

[1]) In F. S. A. de Clercq's *"Nieuw plantkundig woordenboek voor Neder-landsch-Indië"*, Amsterdam 1910, p. 233, *Salam* is stated to be derived from *Eugenia polyantha*, Wight.

[2]) Report of Schimmel & Co. April 1911, 123.

[3]) Berichte d. deutsch. pharm. Ges. 18 (1903), 130.

[4]) R. C. Cowley, Chemist and Druggist 81 (1912), 523, 965.

[5]) Hence the statement of a 4 p.c. yield made in the previous edition must be based on an error.

[6]) Chemist and Druggist of Australasia 27 (1912), 271; Report of Schimmel & Co. October 1912, 119.

Properties. The yellowish oil possesses a strong citral odor. $d_{15°}$ 0.895 to 0.900; optically inactive; $n_{D20°}$ 1.486 to 1,488 (three determinations); soluble in $^1/_2$ to 3 vol. of 70 p.c. alcohol; citral content about 95 p.c.

Composition. The oil is one of the first in which the presence of *citral* was established[1]). In addition to citral, small quantities of other substances are present which impart the characteristic odor peculiar to this oil[2]).

The Eucalyptus Oils.

Origin. The genus *Eucalyptus* (family *Myrtaceæ*) distinguished by its numerous species, is one of the most characteristic representatives of the Australian flora. Because of the few demands it makes upon the soil, and because of its rapid growth, it has been transplanted to other continents. In marshy districts, the haunts of malaria, the eucalyptus tree renders great service because of the rapidity with which it drains the soil. (Comp. p. 244). Hence it is also known as fever tree. As reported by E. de Wildeman[3]) the first specimens made their appearance in Europe in the botanical garden of Naples about the beginning of the 19th century. It was not, however, until the close of the sixties that its importance as a forest tree was recognized. Into France the eucalypts were introduced in 1854 and their culture spread gradually into the territories bordering on the Mediterranean. At the same time, the French took the tree, more particularly *E. Globulus,* to their colonies in northern Africa where large plantations are to be found at the present time. Since 1870 the cultivation of *E. rostrata,* Schlecht., has been conducted intensively. Other species have been planted in private gardens and are but of limited importance in the plan-

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[1]) Bericht of Schimmel & Co. April 1885, 20 and October 1888, 17; comp. also Report of Schimmel & Co. April 1905, 83.

[2]) J. C. Umney and C. T. Bennett, Chemist and Druggist 68 (1906), 738.

[3]) *Notices sur des plantes utiles ou intéressantes de la flore du Congo,* Brussels 1903 I. 175 to 221.

tations. In the East Indies the cultivation was begun in 1863.
The greatest success has been recorded in the Nilgiris. At the
present time Australia, India, Algeria and several other Mediter-
ranean countries are the principal producers. North America,
where the tree was planted immediately after its introduction
into France, also promises well. Finally, the English colonies
of South Africa should be mentioned. The English and German
colonies of tropical Africa, also the Congo State cultivate the
eucalyptus tree with success. In the lower Congo and Katanga
E. Globulus is being favored. In German East Africa and German
Southwest Africa four species are being tried out: — *E. loxophleba,*
Benth., *E. redunca,* Schau., *E. salmonophloia,* F. v. M., and
E. salubris, F. v. M.

Next to the palms the eucalypts are probably the most
useful trees. They serve as shade trees and as windbreaks;
they yield gum, resin, honey; they serve as lumber, fuel and
in the production of oil. As a result of their rapid growth all
of these useful products can be attained in a relatively short
time. More recently caoutchouc has been found in some of the
species, even in the leaves.

Almost all species of *Eucalyptus* contain volatile oil in their
leaves, certain species even in relatively large amount. Although
the eucalyptus oils contain a wide range of chemical substances,
certain regularities as to distribution in the several species
have been observed. According to R. T. Baker and H. G. Smith[1]
it is possible even to prejudge the principal constituents from
the venation of the leaves. They differentiate, mainly, between
three groups. The oil of the first group, the leaves of which
have a thick midrib and the marginal veins of which are very
close to the margin itself, contain principally pinene, but neither
eucalyptol nor phellandrene. In the second, eucalyptol-containing
group the midrib is less prominent and the marginal veins recede
somewhat. The venation of the third, phellandrene-containing

[1] A Research on the Eucalypts especially in regard to their Essential Oils.
Sydney 1902. The description of the eucalyptus oils contained in this treatise
is based on the above-mentioned monograph. The arrangement of the oils
is according to B. and S. which, however, is defective in many respects.
For purpose of reference the title of this monograph, enhanced by numerous
illustrations, is abridged as "Research, p. . . . .".

group is very different; the midrib is very thin and the pennate venation is wanting.

This theory, however, is not supported by all experts. Thus, J. H. Maiden[1]) maintains that neither volatile oil nor manna and kino are essential characteristics, but accessory and adaptive, hence, they should not be used alone but as mere accessories in the chemical diagnosis. The botanical classification for the nomenclature of genera, species and varieties should be based on morphological characteristics. It is on these principles that the large, purely botanical work of J. H. Maiden, "A Critical Revision of the genus Eucalyptus" (Sydney) with numerous plates is based[2]).

Production. The Australian eucalyptus oil industry was first established (1854) in Victoria by Bosisto (Comp. vol. I, p. 167). From there it spread to southern Australia, then to Tasmania and Queensland. In Victoria the principal places of production are Melbourne aud the surrounding country, the shores of Lake Hindmarsh, and Bendigo; in South Australia, Adelaide, Punelroo on the Murray and in the Kangaroo islands; in Queensland Brisbane, Gladstone, Rockhampton, Inghamstown and Wallaroo; in Tasmania, Hobart and Spring Bay.

In Australia the leaves of the several species used for distillation are not always kept separate with sufficient care, hence the botanical designation of a commercial oil is not always reliable.

As a rule the distillation is carried out in a rather primitive fashion. Frequently cubical iron containers of 400 gals. (about 1500 l.) capacity supplied with a cover that can be screwed on, are converted into a readily portable still. The material to be distilled rests on a false bottom, supported about 22 cm. from the bottom of the still, so that it is not brought into contact with the water itself. Heat is supplied by direct fire. The vapors pass through a tube 5 cm. in diameter into the condenser. Occasionally larger stills are met with, namely of from 800 to 2000 gals. capacity. These are made of wood and for distilllation

[1]) Journ. and Proceed. Royal Soc. of N. S. W. 36 (1902), 315; Report of Schimmel & Co. October 1903, 37.

[2]) Up to the present time two volumes have appeared.

steam, generated in a separate boiler, is used. The crude oil is not serviceable as such but must be treated with sodium hydroxide and rectified for the purpose of removing saponifiable substances and the irritating aldehydes which induce coughing. However, the complete destruction of the readily volatile aldehydes is not thus accomplished. The oil thus rectified is the common eucalyptus oil of commerce. About ten per cent. of the oil remains behind with the caustic soda as a kind of soap of a dark brown color and syrupy consistence. This residue known as "eucalyptus tar" or "resin oil", is used as a cheap disinfectant or for perfuming ordinary soaps. Not infrequently it is discarded.

The yield of oil obtained from the several species varies greatly as is revealed by the accompanying table taken from the publications of Baker and Smith.

Compared with the oil production of Australia, that of other countries is small. Toward the close of the past century fairly large amounts of Globulus oil were distilled in Algeria[1]). At present however, the distillation seems to have ceased altogether. The Portuguese oil[2]), which appeared in the market for a time, has also disappeared. Small distilleries, which produce for home consumption, exist in southern France (Fig. 18), in Italy[3]), in India (in the Nilgiris[4])), in Transvaal[5]), and in Mexico[6]). In all of these countries the leaves of the *Eucalyptus Globulus* are distilled. In California, where a number of *Eucalyptus* species are cultivated[7]), the leaves, which are obtained as a by-product when the Globulus trees are felled, are distilled for their oil[8]) yielding about 0.3 p.c. It is used mostly for medicinal purposes.

[1]) Report of Schimmel & Co. October 1897, 27; October 1901, 27; April 1902, 38.

[2]) *Ibidem* October 1897, 27; April 1904, 51; October 1904, 31.

[3]) Chem. Ztg. 30 (1906), 1083.

[4]) Report of Schimmel & Co. April 1891, 34; April 1907, 52.

[5]) *Ibidem* April 1909, 53; October 1909, 67.

[6]) *Ibidem* October 1910, 65.

[7]) N. D. Ingham, Bulletin No. 196 of the Agricultural Experiment Station in Berkeley; Journ. d'Agriculture tropicale 10 (1910), 91.

[8]) F. Rabak, Americ. Perfumer 5 (1910), 220.
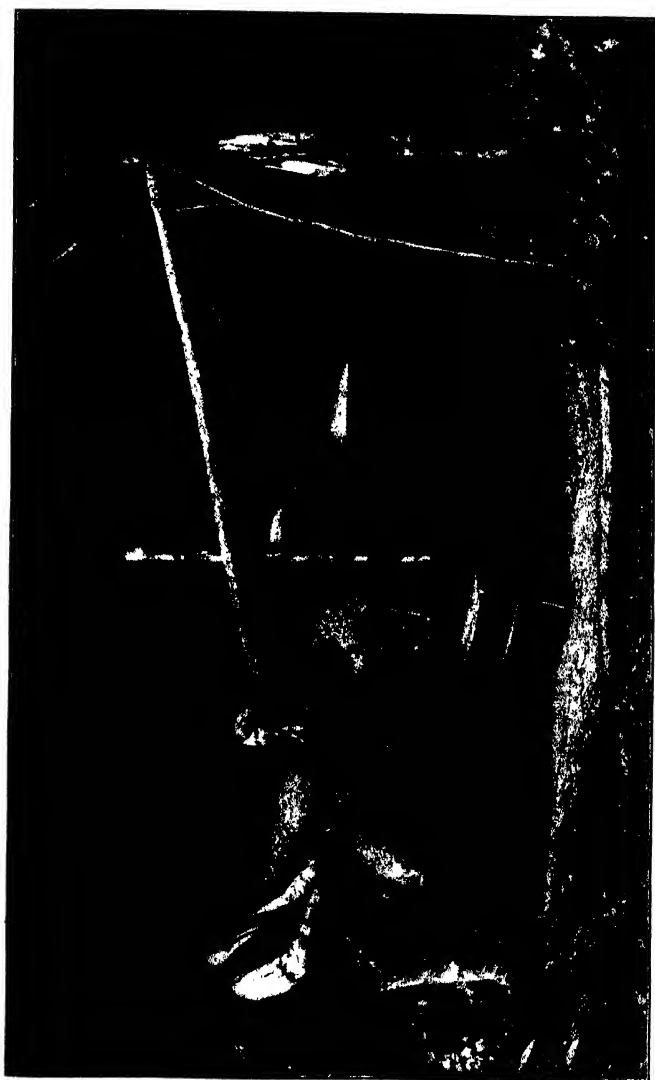
Fig. 18. Eucalyptus oil distillation in Southern France.

Table of oil yield[1]) of different species of *Eucalyptus* beginning with the lowest yield and ending with the highest.

	Yield in p.c.		Yield in p.c.
E. obtusifolia und *Thozetiana*		*E. Luehmanniana*	0.289
exceedingly small		„ *stellulata*	0.293
„ *rubida*	0.0084	„ *Fletcheri*	0.294
„ *gomphocephala*	0.031	„ *Rudderi*	0.309
„ *aggregata*	0.04	„ *macrorhyncha* . . . up to	0.31
„ *nigra*	0.041	„ *Baeuerleni*	0.328
„ *siderophloia*	0.056	„ *punctata* var. *didyma* up to	0.37
„ *corymbosa*	0.06	„ *hemilampra*	0.375
„ *Planchoniana*	0.06	„ *Gunnii*	0.387
„ *acmenioides*	0.089	„ *Stuartiana*	0.394
„ *capitellata*	0.1	„ *rostrata* . . . . . up to	0.4
„ *albens*	0.101	„ *sideroxylon* var. *pallens* .	0.4035
„ *paniculata*	0.104	„ *resinifera*	0.414
„ *melanophloia* . . .	0.105	„ *Woollsiana*	0.4435
„ *botryoides*	0.106	„ *coriacea*	0.452
„ *Macarthuri*	0.112	„ *eximia*	0.462
„ *fastigata*	0.115	„ *microtheca*	0.478
„ *intermedia*	0.125	„ *Rodwayi*	0.482
„ *carnea*	0.155	„ *tereticornis*	0.482
„ *umbra*	0.155	„ *Sieberiana*	0.494
„ *crebra*	0.159	„ *stricta*	0.494
„ *robusta*	0.161	„ *nova-anglica*	0.5013
„ *tessellaris*	0.162	„ *microcorys*	0.51
„ *Dawsoni*	0.172	„ *bicolor*	0.52
„ *pilularis* . . . . up to	0.176	„ *longifolia*	0.535
„ *angophoroides*	0.185	„ *lactea* . . . . . up to	0.573
„ *acaciaeformis*	0.197	„ *hemiphloia*	0.575
„ *trachyphloia*	0.2	„ *ovalifolia* var. *lanceolata* .	0.579
„ *acervula*	0.212	„ *citriodora*	0.586
„ *maculata*	0.228	„ *conica*	0.587
„ *propinqua*	0.235	„ *coccifera*	0.609
„ *marginata* . . . up to	0.24	„ *Behriana*	0.614
„ *paludosa*	0.243	„ *intertexta* . . . . up to	0.64
„ *calophylla*	0.248	„ *squamosa*	0.644
„ *patentinervis*	0.254	„ *apiculata*	0.65
„ *saligna* var. *pallidivalvis* up to	0.255	„ *laevopinea*	0.66
„ *affinis*	0.259	„ *taeniola*	0.66
„ *ovalifolia*	0.27	„ *quadrangulata*	0.68
„ *haemastoma*	0.278	„ *viminalis* var. *a*	0.7005

[1]) In all cases where several yields are recorded in literature the highest percentage only is given.

	Yield in p.c.		Yield in p.c.
E. Rossii	0.719	*E. Maideni*	1.007
„ *viminalis* . . . . up to	0.74	„ *viridis*	1.06
„ *sideroxylon*	0.743	„ *maculosa*	1.061
„ *Bridgesiana* . . . up to	0.75	„ *oleosa*	1.064
„ *obliqua* . . . . . up to	0.77	„ *Stuartiana* var. *cordata* .	1.13
„ *piperita*	0.78	„ *urnigera*	1.13
„ *tereticornis* var. *linearis* .	0.783	„ *oreades*	1.16
„ *virgata*	0.79	„ *punctata* . . . . up to	1.19
„ *eugenioides* . . . up to	0.795	„ *rostrata* var. *borealis* up to	1.191
„ *vernicosa*	0.807	„ *dextropinea* . . . up to	1.2
„ *regnans* . . . . up to	0.82	„ *redunca*	1.205
„ *diversicolor*	0.825	„ *Andrewsi*	1.27
„ *polyanthema*	0.825	„ *Muelleri*	1.28
„ *Cambagei* . . . . up to	0.835	„ *cinerea* . . . . . up to	1.3
„ *pendula*	0.843	„ *camphora* . . . . up to	1.34
„ *dextropinea* . . . . up to	0.850	„ *polybractea*	1.35
„ *campanulata*	0.851	„ *Risdoni*	1.35
„ *populifolia* . . . up to	0.856	„ *salubris*	1.391
„ *dealbata*	0.857	„ *odorata*	1.4
„ *melliodora*	0.866	„ *salmonophloia*	1.44
„ *unialata*	0.897	„ *vitrea*	1.48
„ *Baileyana*	0.9	„ *Morrisii* . . . . up to	1.69
„ *gracilis*	0.901	„ *Smithii* . . . . up to	1.78
„ *Globulus* . . . . (fresh)	0.918	„ *linearis* . . . . up to	1.8
„ *occidentalis*	0.954	„ *radiata* . . . . up to	1.88
„ *goniocalyx*	0.959	„ *delegatensis* . . . up to	1.94
„ *Bosistoana*	0.968	„ *pulverulenta*	2.22
„ *Wilkinsoniana*	0.975	„ *cordata*	2.32
„ *fraxinoides*	0.985	„ *dives* . . . . . up to	2.89
„ *dumosa* . . . . . ca.	1	„ *Globulus* . . . (dry) up to	3
„ *Perriniana* . . . . . ca.	1	„ *Staigeriana* . . . up to	3.36
„ *phlebophylla* . . . . ca.	1	„ *amygdalina*	4.215

Adulteration. Inasmuch as the eucalyptus trees grow mixed in the production areas of Australia, the commercial oils are rarely the product of a single species. Moreover, the oils are mixed in order to secure a definite eucalyptol content or for the purpose of cheapening a given oil. Inasmuch as the cineol content of the cineol-containing oils is universally regarded as the measure of value, the cineol assay is unavoidable in passing judgment on an oil. For the methods employed see vol. I, p. 600.

On account of the low price of eucalyptus oil, adulterations proper have been observed but rarely. In an oil with a high

specific gravity and a relatively low cineol content, C. T. Bennett[1] found castor oil. When the oil in question was distilled in vacuum the castor oil remained behind and could be recognized by its high S. V. and its behavior toward petroleum ether.

Uses. Originally eucalyptus oil was used exclusively for medicinal purposes. It is still used as a domestic remedy: for embrocations, inhalations, as vermifuge and for similar purposes The amounts thus used are considerable, more particularly in Australia where a bottle of eucalyptus oil is to be found in every household. In Europe the Globulus oils rich in cineol are preferred to those containing phellandrene. As to whether cineol or phellandrene, or some other constituent is the pharmacologically valuable ingredient of the oil, there exists a difference of opinion[2] In this connection reference should be made to a publication by C. Hall[3] on the therapeutic value of eucalyptus oils with special reference to their antiseptic value from the Pathological Institute of the University of Sydney.

A large part of eucalyptus oil is consumed in the production of eucalyptol, but still larger amounts are used in the Australian mines for the flotation of lead and zinc sulphides from admixed rock. Inasmuch as the phellandrene-containing oils are best adapted to this purpose, this process will be described under the principal representative of this group, the *Eucalyptus amyg-dalina* (see p. 278). Not to be underestimated are the amounts of the cheaper phellandrene-containing oils used in ordinary soaps

The individual oils hereinafter described are arranged according to the classification of Baker and Smith as carried out in their monograph already alluded to. The following groups[4] are recognized by them: —

[1] Chemist and Druggist 66 (1905), 33.

[2] *Ibidem* 76 (1910), 271, 669. — Evans Sons Lescher and Webb Ltd. Analytical Notes 1910. — Chemist and Druggist of Australasia 27 (1912), 396. — Report of Schimmel & Co. October 1910, 66; April 1911, 72; April 1914, 61 The two last references deal with the use of eucalyptus oil in scarlet fever and measles.

[3] On eucalyptus oils especially in relation to their bactericidal power Parramatta, N. S. W. 1904; Report of Schimmel & Co. October 1904, 37.

[4] This classification cannot always be carried out strictly. Occasionally an oil will be found which should be arranged with another group.

I. Phellandrene-free oils, which consist for the main part of pinene with little or no cineol.

II. Oils which consist principally of pinene and cineol, the cineol content of which, however, does not exceed 40 p.c. Phellandrene is absent.

IIIa. Phellandrene-free oils consisting principally of cineol and pinene, the cineol content of which exceeds 40 p.c.

IIIb. Oils containing more than 40 p.c. cineol, which contain less pinene but in which aromadendral occurs.

IIIc. Oils with more than 40 p.c. cineol containing phellandrene.

IV. Oils with not more than 30 p.c. cineol and devoid of phellandrene, which consist principally of cineol, pinene and aromadendral.

V. Oils which consist of pinene, cineol and phellandrene and which contain not more than 30 p.c. cineol.

VIa. Oils which consist principally of phellandrene, cineol (up to 30 p.c.) and piperitone.

VIb. Oils which consist principally of phellandrene and piperitone and in which little or no cineol is to be found.

VII. This group comprises all of those oils which cannot be classified with any of the previous groups.

Group I.

Phellandrene-free oils, which consist for the main part of pinene with little or no cineol.

519. Oil of Eucalyptus tesselaris.

Eucalyptus tesselaris, F. v. M. (*E. Hookeri*, F. v. M.) occurs on the north coast and its "hinterland" of New South Wales, also in Queensland, South Australia and in the northern part of Australia. It is known as Moreton bay ash or Carbene. The leaves contain 0.162 p.c. of oil[1]. $d_{15°}$ 0.8757; $d_{16°}$ 0.8962[2]); $[\alpha]_D + 9.82°$; $n_{D16°}$ 1.4881[2]); A.V. 0.8; E.V. 5.4; with 10 vol. of

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[1]) Research, p. 22. — Report of Schimmel & Co. April 1898, 38.

[2]) Smith, Journ. and Proceed. Royal Soc. of N. S. W. 39 (1905), 46; Report of Schimmel & Co. April 1906, 33. In this paper the solubility and the index of refraction of a number of eucalyptus oils are described and an attempt made to classify the oils in accordance with there properties.

80 p.c.[1]) alcohol it forms a turbid solution. The oil possesses a distinct odor of *cymene* and contains *pinene*[2]), a small amount of *cineol*, also *aromadendrene*[3]). Phellandrene could not be detected.

520. Oil of Eucalyptus trachyphloia.

Eucalyptus trachyphloia, F. v. M.[4]) is one of the species known as "bloodwood" and is found in certain parts of New South Wales and Queensland. The leaves contain about 0.2 p.c. of oils the odor of which reminds of that of turpentine oil also of that of cinnamon oil. $d_{15°}$ 0.8929; $[\alpha]_D$ + 10.9°; $n_{D15°}$ 1.4901[5]); A.V. 1.08; E.V. 2.05; with 10 vol. of 80 p.c. alcohol it does not form a clear solution. The principal constituents of the oil are *pinene* and *aromadendrene*. In addition *aromadendral*, also traces of *cineol*, but no phellandrene were found.

521. Oil of Eucalyptus corymbosa.

Eucalyptus corymbosa, Sm. also known as "bloodwood" is a tall tree, readily recognized, that grows in the coast regions of New South Wales, also in Victoria, Queensland and northern Australia[6]). The leaves yield only 0.06 p.c. of a light yellow oil: $d_{15°}$ 0.883; d 0.881[7]); $d_{16°}$ 0.8867[5]); $[\alpha]_D$ — 9.5°; $n_{D15°}$ 1.4895[5]); A.V. 1.8; E.V. 2; not soluble in 10 vol. of 80 p.c. alcohol. It consists principally of *pinene* and contains but little *cineol*, no phellandrene[6]) and some *aromadendral*[5]). According to Wittstein and Mueller the odor of the oil reminds faintly of lemons and roses (?) and has a bitter, somewhat camphoraceous taste[7]). According to Schimmel & Co.[8]) it is rich in cineol.

[1]) All solubility statements made by Baker and Smith are based on *weight* percentages.

[2]) As to the pinenes of the eucalyptus oils, see Research, p. 238.

[3]) See p. 293.

[4]) Research, pp. 23, 246.

[5]) Smith, *loc. cit.* 46.

[6]) Research, p. 25. — Report of Schimmel & Co. April 1898, 38.

[7]) J. H. Maiden, The useful native plants of Australia. London and Sydney, 1889, p. 266.

[8]) Report of Schimmel & Co. April 1893, 38.

522. Oil of Eucalyptus intermedia.

Eucalyptus intermedia, R. T. Baker, which occurs in spots in New South Wales is also known as "bloodwood" or "bastard bloodwood". The oil (yield 0.125 p.c.) is an amber-yellow liquid of a faint odor; specific gravity 0.8829 to 0.8881 at 15°; $[\alpha]_D$ + 11.2 to + 13.7°; $n_{D16°}$ 1.4878[1]); A.V. 1.1; E.V. 1.4 to 3.8. It consists principally of *pinene,* contains a trace of *cineol,* possibly *aromadendral*[1]), but no phellandrene[2]).

523. Oil of Eucalyptus eximia.

Known as "white" or "yellow" bloodwood, *Eucalyptus eximia,* Schauer occurs in the coastal ranges of New South Wales. Its leaves yield 0.462 p.c. of volatile oil, which, in the crude condition, is orange-brown and has an odor of turpentine; $d_{15°}$ 0.8998; $[\alpha]_D$ + 32.01°; $n_{D16°}$ 1.4889[1]); A.V. 1.1; E.V. 3.4; with 10 vol. of 80 p.c. alcohol it yields no clear solution. It consists almost exclusively of *pinene* and *aromadendrene.* Neither cineol nor phellandrene are contained therein[3]).

524. Oil of Eucalyptus botryoides.

Eucalyptus botryoides, Sm. (*E. platypoda,* Cav.) known as "bastard mahogany" or "bangalay", occurs along the coast from Victoria to Queensland. According to Baker and Smith[4]), the oil (yield 0.106 p.c.) does not possess a pleasant odor. It is a mobile liquid and reddish-brown in the crude condition. The principal constituent is a d-*α-pinene.* It also contains *aroma-dendrene* and·traces of *cineol,* but no phellandrene. Pinene was identified by means of its nitrosochloride. Its constants, determined on two samples, are: $d_{15°}$ 0.8778 and 0.8774; $n_{D16°}$ 1.4787[5]); A.V. 7.3 and 4.1; E.V. 14.1 and 11.1; soluble in 7 to 9 vol. of 80 p.c. alcohol; 87 p.c. of the oil boils between 161 and 190°; $[\alpha]_D$ + 27.2ʼ.

[1]) Smith, *loc. cit.* 46.
[2]) Baker and Smith, Research, p. 27.
[3]) *Ibidem,* pp. 28, 246.
[4]) *Ibidem,* p. 29.
[5]) Smith, *loc. cit.* 45.

525. Oil of Eucalyptus robusta.

The leaves of *Eucalyptus robusta*, Sm. (*E. rostrata*, Cav.), known as swamp mahogany, and growing along the coast from Victoria to Queensland, yield 0.161 p.c. of oil. The crude product is red and has a turpentine-like odor: $d_{15°}$ 0.8777; $[\alpha]_D$ + 4.56°; $n_{D18°}$ 1.4801[1]); A. V. 2.7; E. V. 6.4; soluble in 8 vol. of 80 p.c. alcohol. The oil consists principally of *pinene*, also of *aromadendrene*[1]), with traces of *cineol* and *phellandrene*[2]).

526. Oil of Eucalyptus saligna var. pallidivalvis.

Flooded gum is the common name for *Eucalyptus saligna*, Sm. var. *pallidivalvis*, Baker et Smith, a tree that occurs in various parts of New South Wales. The oil yield is 0.121 to 0.255 p.c. and ist dark red[3]): $d_{15°}$ 0.8860 to 0.8937; $[\alpha]_D$ + 37.14 to 39.59°; A. V. 9.9; E. V. 19; E. V. after acetylation 56.04; soluble in 7 to 9 vol. of 80 p.c. alcohol. The principal constituent is d-*α-pinene* (characterized by its nitrosochloride). In addition there occur the *amyl ester* of *eudesmic acid*, little *cineol*, a free *alcohol* and a *valeric ester*. Phellandrene does not occur[4]).

527. Oil of Eucalyptus nova-anglica.

Eucalyptus nova-anglica, Deane et Maiden occurs widely distributed in New South Wales, more particularly in the New England district. It is known as "black peppermint" or as "broad-suckered peppermint" although it does not contain a single constituent the odor of which reminds of peppermint[5]). Yield 0.5 p.c.; color dark; odor strongly turpentine-like; $d_{15°}$ 0.907; $[\alpha]_D$ + 16°; $n_{D16°}$ 1.4900[6]); A. V. 3.3; E. V. 1.8; does not form a clear solution with 10 vol. of 80 p.c. alcohol. In a later contri-

[1]) Smith, *loc. cit.* 47.
[2]) Research, p. 31.
[3]) The red color of most of the crude eucalyptus oils is caused by the iron of the stills which is dissolved by the free acid present in the oil.
[4]) Research, pp. 32, 249, 251.
[5]) *Ibidem*, pp. 34, 246.
[6]) Smith, *loc. cit.* 46.

bution[1]) the following constants have been recorded: d_{16}. 0.9221 to 0.9301; $\alpha_D + 0.9$ to $+ 5.8°$; $n_{D15°}$ 1.4892 to $n_{D20°}$ 1.4932; S. V. 5.7 to 6.9. The principal constituent of the oil is *pinene*[2]). *Phellandrene* is occasionally found in very small quantities, the *cineol* content is low. Aromadendrene is present in large amount[1]).

528. Oil of Eucalyptus umbra.

Bastard white mahogany, *Eucalyptus umbra,* R. T. Baker, one of the so-called stringybarks, so called because of the fibrous character of the bark, is a tree found in spots in New South Wales. The oil described by Baker and Smith[3]) was obtained with a yield of 0.155 to 0.169 p.c. and constitutes an orange-yellow liquid rich in d-*pinene* with traces of *cineol* but no phellandrene. $d_{15°}$ 0.8963; $[\alpha]_D + 41.5°$; E.V. 35.8; soluble in 7 vol. of 80 p.c. alcohol. It contains acetic acid esters and some valeric acid, an acid that seems to occur in almost all eucalyptus oils. Nothing is known about the alcohol underlying the esters.

529. Oil of Eucalyptus dextropinea.

To the stringybarks there also belongs *Eucalyptus dextropinea,* R. T. Baker, which is found in certain localities in New South Wales. Baker and Smith[4]) distilled the oil from the fresh leaves with a yield of 0.825 to 0.850 p.c. The dark red, strongly dextrogyrate oil has a specific gravity of 0.8743 to 0.8763 at 17°; $n_{16°}$ 1.4741[5]); S. V. 22.9; with 10 vol. of 80 p.c. alcohol it does not form a clear solution. For an oil distilled later with a yield of 1.02 p.c. the authors[6]) record the following

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[1]) Journ. and Proceed. Royal Soc. of N. S. W. **45** (1911), 285; Report of Schimmel & Co. October 1912, 64.

[2]) Research, pp. 34, 246.

[3]) Research, p. 35.—Baker, Proceed. Linnean Soc. of N. S. W. **1900**, 687; Report of Schimmel & Co. April 1902, 40. See also Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 269.

[4]) Journ. and Proceed. Royal Soc. of N. S. W. **32** (1898), 195.—Research, pp. 38, 238.

[5]) Smith, *loc. cit.* 45.

[6]) Journ. and Proceed. Royal Soc. of N. S. W. **45** (1911), 283; Report of Schimmel & Co. October 1912, 64.

properties: $d_{15°}$ 0.8831; α_{D} + 24.2°; $n_{D21°}$ 1.4688; S. V. 22.1; soluble in 10 vol. of 80 p.c. alcohol. After rectification by steam distillation the almost colorless oil had the following properties: $d_{15°}$ 0.8698; α_{D} + 24.4°; $n_{D22°}$ 1.4647. When fractioned 62 p.c. came over between 156 and 162°, 25 p.c. between 162 and 172°[1]).

The oil consists almost exclusively of d-α-pinene. After refractionation, the principal fraction boiled between 156 and 157°; $d_{16°}^{16°}$ 0.8629; $[\alpha]_{D}$ + 41.2° at 18°. α-Pinene was identified by the preparation of its nitrosochloride (m. p. 103°), of nitrosopinene (m. p. 128 to 129°), also of terpin hydrate and of pinene monohydrochloride (m. p. 121 to 124°).

In addition to α-pinene this oil contains small amounts of *cineol*, which was identified in the higher boiling portions by its behavior toward iodol and bromine, also 3.7 p.c. of *geranyl acetate*[2]).

530. Oil of Eucalyptus Wilkinsoniana.

Small-leaved stringybark, *Eucalyptus Wilkinsoniana*, R. T. Baker (*E. hæmastoma*, F. v. M., *E. lævopinea*, var. *minor*, R. T. Baker) grows in isolated places in New South Wales. Baker and Smith[3]) obtained 0.975 p.c. of oil: $d_{15°}$ 0.8944; $[\alpha]_{D}$ − 23.9°; $n_{D16°}$ 1.4774[2]); A. V. 2.67; E. V. 2.33; it does not yield a clear solution with 10 vol. of 80 p.c. alcohol. l-*Pinene* is the principal constituent. Only traces of *cineol* are present. The presence of phellandrene cannot always be proven. Its occurrence seems to be dependent on the season.

Not less than 80 p.c. of the oil distils over below 170°.

531. Oil of Eucalyptus lævopinea.

From the fresh leaves of silvertop stringybark, *Eucalyptus lævopinea*, R. T. Baker, which occurs only in a few places in

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[1]) Journ. and Proceed. Royal Soc. of N. S. W. 32 (1898), 195. — Research, p. 38, 238.

[2]) Smith, *loc. cit.* 45.

[3]) Research, p. 39. — R. T. Baker, Proceed. Linnean Soc. of N. S. W. 1900, 678; Report of Schimmel & Co. April 1902, 40.

New South Wales, Baker and Smith[1]) obtained 0.66 p.c. of a red oil with the following properties: $d_{15°}$ 0.8755; $n_{D16°}$ 1.4769[2]); S. V. 7.0; does not yield a clear solution with 10 vol. of 80 p.c. alcohol. For another oil distilled later the authors[3]) report the following properties: $d_{15°}$ 0.8875 and 0.8871; α_D — 30.7 to — 33.3°; $n_{D19°}$ 1.4691 to 1.4697. Upon fractionation 60 p.c. came over between 157 and 164° and 28 p.c. between 164 and 172°[1]). Whereas the oil of *Eucalyptus dextropinea* consists almost exclusively of *d-α-pinene* that of *E. lævopinea* consists almost exclusively of *l-α-pinene*[4]). Fraction 157 to 158°, which may be regarded as almost pure pinene, had $d_{16°}^{19°}$ 0.8626; $[\alpha]_D$ — 48.63 . It was identified by means of the same derivatives prepared in connection with the oil of *Eucalyptus dextropinea*. In addition to *l-pinene* the oil contains about 5 p.c. *cineol*[3]).

532. Oil of Eucalyptus calophylla.

According to Baker and Smith[5]) *Eucalyptus calophylla,* R. Br., red gum, is indigenous to western Australia and in its general appearance closely resembles the bloodwood of eastern Australia. The oil was obtained with a yield of 0.248 p.c., was dark red in the crude condition and had the following properties: $d_{16°}$ 0.8756; α_D + 22.9°; $n_{D16°}$ 1.4788; E. V. 10.51; does not form a clear solution with 10 vol. of 80 p.c. alcohol. d-*Pinene* is the dominant constituent. Judging from the constants and the odor, *cymene* is present, also *aromadendrene,* traces of *cineol* and small amounts, of *acetic esters.* Phellandrene, aromadendral and piperitone are wanting.

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[1]) Journ. and Proceed. Royal Soc. of N. S. W. 32 (1898), 202; Report of Schimmel & Co. April 1899, 24. — Research, p. 41, 242.

[2]) Smith, *loc. cit.* 45.

[3]) Journ. and Proceed. Royal Soc. of N. S. W. 45 (1911), 278; Report of Schimmel & Co. October 1912, 63.

[4]) According to Smith practically all of the oils obtained from species related to *Eucalyptus Globulus* contain pinene, such as the oils of *E. Bridgesiana, E. goniocalyx,* etc.

[5]) Pharmaceutical Journ. 75 (1905), 356.

533. Oil of Eucalyptus carnea.

Eucalyptus carnea (*E. umbra*, R. T. Baker part.) a species described by R. T. Baker[1]) is restricted, in its occurrence, to New South Wales. It yielded 0.155 p.c. of volatile oil, the principal constituent of which is d-*α-pinene*. Of *cineol* it contains only about 5 p.c., whereas the presence of phellandrene could not be detected. Nothing is recorded as to the properties of the oil.

534. Oil of Eucalyptus diversicolor.

Eucalyptus diversicolor, F. v. M. (*E. colossea*, F. v. M.)[2]) is indigenous to western Australia, where it is known as karri, and occasionally attains the respectable height of 400 ft. This species has also been planted in Ceylon and Algeria[3]). Baker and Smith[4]) obtained 0.825 p.c. of a light lemon-yellow oil having the following properties: $d_{15°}$ 0.9145; $\alpha_D + 30.1°$; $n_{D16°}$ 1.4747; E. V. 53.2; not soluble in 10 vol. of 70 p.c. alcohol, but soluble in an equal volume of 80 p.c. alcohol. It consists principally of d-*pinene*, about 20 p.c. of an *acetate*, and traces of *cineol*. Phellandrene was not found.

W. P. Wilkinson[3]) who had previously examined the oil, reports $d_{15°}$ 0.924; $[\alpha]_D + 9.7°$.

535. Oil of Eucalyptus acaciæformis.

Eucalyptus acaciæformis, Deane et Maiden is known as "red" or "narrow-leaved peppermint". It occurs throughout New South Wales (New England). Baker and Smith[5]) obtained 0.197 p.c. of an oil with a turpentiny odor which, in the crude condition, was brown; $d_{15°}$ 0.8864; $\alpha_D + 35.7°$; $n_{D20°}$ 1.4713; insoluble in 10 vol. of 80 p.c. alcohol. Its principal constituent is d-*pinene*. In addition it contains *aromadendrene*, presumably also *geranyl acetate*.

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[1]) Proceed. Linnean Soc. of N. S. W. 1906, 303; Report of Schimmel & Co. April 1907, 52.

[2]) See also Maiden, A critical revision of the genus Eucalyptus. vol. II. p. 298.

[3]) Proceed. Royal Soc. of Victoria 1893, 198.

[4]) Pharmaceutical Journ. 75 (1905), 356.

[5]) Journ. and Proceed. Royal Soc. of N. S. W. 45 (1911), 271; Report of Schimmel & Co. October 1912, 63.

Group II.

Oils which consist principally of pinene and cineol,
the cineol content of which, however, does not
exceed 40 p.c.   Phellandrene is absent.

536. Oil of Eucalyptus occidentalis.

The oil of *Eucalyptus occidentalis*, Endl., received early
mention from Wilkinson. Later it was described in greater
detail by Baker and Smith[1]). The leaves of this West Australian
species, known as mallet gum, yield 0.954 p.c. of an oil which
is reddish in the crude condition, is free from phellandrene,
contains 36 p.c. *cineol*, relatively much *sesquiterpene*, also
d-*pinene* and small amounts of *aromadendral*. $d_{15°}$ 0.9135;
α_D + 9.0°; $n_{D16°}$ 1.4774;   E. V. 2.48; not soluble in 10 vol. of
70 p.c. alcohol, but forms a clear solution with an equal
volume of 80 p.c. alcohol.   Wilkinson records: d 0.9236;
$[\alpha]_D$ + 2.7°.

537. Oil of Eucalyptus redunca.

The white gum or "wandoo" of western Australia, *Eucalyptus
redunca*, Schauer, has been examined by Baker and Smith[2]).
The yield of oil is 1.205 p.c. The color of the crude oil is red,
the rectified oil is colorless. The odor of pinene predominates,
but that of cineol is also noticeable. $d_{15°}$ 0.9097; α_D + 13.5°;
$n_{D16°}$ 1.4720[3]);   E. V. 2.4;   soluble in 6 vol. of 70 p.c. alcohol.   It
contains d-*pinene* also about 40 p.c. of *cineol* and traces of
ester. The higher boiling fraction (about 3 p.c.) consists of
aromadendrene. The test for phellandrene gave negative results.

The oil distilled from the suckers[4]) had the same properties
as did that of the older branches.

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[1]) Pharmaceutical Journ. 75 (1905), 358.

[2]) *Ibidem* 357.

[3]) Smith, *loc. cit.* 45.

[4]) As is well known, the young shoots of the eucalypts frequently have
differently shaped leaves than the older branches.

538. Oil of Eucalyptus Bæuerleni.

Eucalyptus Bæuerleni, F. v. M., brown gum, inhabits the difficultly accessible parts of Sugar Loaf Mountain in New South Wales. Baker and Smith[1]) report the following data concerning the oil: yield 0.328 p.c.; color light yellow; $d_{15°}$ 0.8895; $[\alpha]_D + 4.55°$; $n_{D16°}$ 1.4841[2]); S. V. 9.98; soluble in 4 vol. of 80 p.c. alcohol. It contains *pinene, cineol, eudesmol* and *aromadendrene*, but no phellandrene.

539. Oil of Eucalyptus propinqua.

In Queensland *Eucalyptus propinqua*, Deane et Maiden is known as grey gum. From its leaves Baker and Smith[3]) obtained 0.235 p.c. of an oil which, in the crude condition, was red and possessed the following properties: $d_{15°}$ 0.8989; $[\alpha]_D + 4.9°$; $n_{D16°}$ 1.4788[4]); A. V. 1.2; E. V. 7.2; soluble in 8 vol. of 70 p.c. alcohol. In addition to *cineol*, the presence of *pinene* and *aromadendral* was ascertained. Phellandrene was not present.

540. Oil of Eucalyptus affinis.

Eucalyptus affinis, Deane et Maiden grows in the western districts of New South Wales. According to Baker and Smith[5]) the leaves contain 0.259 p.c. of oil which, in the crude condition, is orange-brown. $d_{15°}$ 0.9259; $[\alpha]_D + 6.05°$; $n_{D16°}$ 1.4921[2]); A. V. 1.9; E. V. 2.79; soluble in an equal volume of 80 p.c. alcohol. It consists principally of *aromadendrene*, also contains *cineol* and *pinene*, but no phellandrene.

541. Oil of Eucalyptus paludosa.

One of the widely distributed species of *Eucalyptus* is *E. paludosa*, R. T. Baker which occurs in many parts of New South Wales, also in Victoria and Tasmania. Its common names

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¹) Research, p. 43.
²) Smith, *loc. cit.* 46.
³) Research, p. 45.
⁴) Smith, *loc. cit.* 45.
⁵) Research, p. 46, 246. For the botanical description see also: Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 101.

are yellow gum, swamp or flooded gum and in Tasmania red gum. Baker and Smith[1]), who obtained 0.243 p.c. of oil, record the following constants: $d_{15°}$ 0.9056 and 0.9023; $[\alpha]_D + 11.0°$ and $+ 15.7°$; $n_{D10°}$ 1.4773[2]); A.V. 3.2 and 1.1; E.V. 15.2 and 16.8; soluble in an equal volume of 80 p.c. alcohol. In addition to *pinene* and *cineol* they found a *sesquiterpene* and a *valerate*. Phellandrene could not be detected. The crude oil was red and had an odor of turpentine.

In this connection mention may be made of an oil of unknown botanical origin which was designated red gum, more particularly red gum of Tenterfield[3]). It came from Portugal: $d_{15°}$ 0.9144; $\alpha_D — 2°38'$; insoluble in 70 p.c. alcohol, soluble in 1 vol. of 80 p.c. alcohol. It had an odor of cuminic aldehyde and contained *cineol*, but was free from phellandrene.

542. Oil of Eucalyptus lactea.

Spotted gum, *Eucalyptus lactea*, R. T. Baker is restricted to certain parts of New South Wales. Baker and Smith[4]) record the following constants for the oil: $d_{15°}$ 0.8826 and 0.8752 for the crude oil and 0.8788 for the rectified oil; $[\alpha]_D — 1.32°$ and $- 0.6°$ (the crude oil is inactive); $n_{D16°}$ 1.4898[5]); A.V. 2.08; E.V. 6.48; soluble in 2 to 5 vol. of 80 p.c. alcohol. The yield amounted to 0.541 and 0.573 p.c. respectively. The crude oil had a red color. *Pinene* and small amounts of *cineol* were found present, but not phellandrene.

543. Oil of Eucalyptus rubida.

Candle bark is the common name for *Eucalyptus rubida*, Deane et Maiden which grows in southern New South Wales. The leaves contain but very little oil, Baker and Smith[6]) obtaining only a 0.0084 p.c. yield; $d_{15°}$ 0.9067; $[\alpha]_D + 3.6°$; $n_{D16°}$ 1.5011[7]);

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[1]) Research, p. 48.

[2]) Smith, *loc. cit.* 45.

[3]) Report of Schimmel & Co. October 1900, 32.

[4]) Research, p. 50. See also Baker, Proceed. Linnean Soc. of N. S. W. 1900, 691; Report of Schimmel & Co. April 1902, 39.

[5]) Smith, *loc. cit.* 46.

[6]) Research, p. 51.

[7]) H. G. Smith, *loc. cit.* 46.

S. V. 3.16; does not yield a clear solution with 10 vol. of 80 p.c. alcohol. *Pinene*, a small amount of *cineol* and *sesquiterpenes* were found present, but not phellandrene.

544. Oil of Eucalyptus intertexta.

Eucalyptus intertexta, R. T. Baker, known as spotted gum, gum, "coolabah", has been found in various places in New South Wales. Baker and Smith[1] obtained 0.2 to 0.64 p.c. of oil with the following constants: $d_{15°}$ 0.9076; $[\alpha]_D + 11.3°$ and 10.7`; $n_{D16°}$ 1.4748[2]); soluble in 1.5 to 2.5 vol. of 70 p.c. alcohol. The crude oil had an orange-yellow color. It contains about 35 p.c. of *cineol*, a relatively large amount of d-*pinene*, also *aromadendrene*. The presence of phellandrene could not be detected.

545. Oil of Eucalyptus maculata.

Eucalyptus maculata, Hooker is one of the spotted gums that occur in New South Wales and Queensland. It has also been cultivated in Ceylon and Algiers[3]). Baker and Smith[4]) report the following data concerning the oil: yield about 0.228 p.c.; $d_{15°}$ 0.9201 and 0.8959; $[\alpha]_D$ ↓ 8.37 and 5.7`; $n_{D16°}$ 1.4861[5]); A.V.4.1; E. V. 5.46 and 6.47; insoluble in 10 vol. of 70 p.c. alcohol, soluble in 1 to 4 vol. of 80 p.c. alcohol. The crude oil contains about 20 p.c. *cineol*, a relatively large amount of *pinene* and *aromadendrene*.

Many years ago Schimmel & Co.[3]) reported on a socalled oil of *Eucalyptus maculata* which had a citronella-like odor. According to Baker and Smith this was, no doubt, derived from *Eucalyptus citriodora*.

546. Oil of Eucalyptus microcorys.

The tallow-wood, *Eucalyptus microcorys*, F. v. M., is distributed along the coast of New South Wales and Queensland.

[1]) Research, p. 52. — Baker, Proceed. Linnean Soc. of N. S. W. 1900, 308; Report of Schimmel & Co. October 1901, 28.

[2]) Smith, *loc. cit.* 45.

[3]) Bericht von Schimmel & Co. April 1888, 19.

[4]) Research, p. 54, 246.

[5]) H. G. Smith, *loc. cit.* 46.

Fig. 19. Eucalyptus tree near Sydney.

Baker and Smith[1]) obtained 0.51 p.c., Maiden 1.96 p.c. of an almost colorless oil from the leaves: d_{15}. 0.895; $[\alpha]_D + 20.45°$; n_{D16}. 1.4747[2]); S. V. 19.6; not soluble in 10 vol. of 70 p.c. alcohol, soluble in 1 vol. of 80 p.c. alcohol. In addition to much d-*α-pinene* (characterized by the customary reactions), the presence of *cineol, aromadendrene* and of *esters,* but not that of phellandrene, was ascertained. Upon standing the cineol content of the oil is said to have increased.

In connection with a commercial product Schimmel & Co. determined the following constants: d_{15}. 0.9038; $\alpha_D + 12°29'$, insoluble in 10 vol. of 70 p.c. alcohol, soluble in 1 to 1.5 vol. and more of 80 p.c. alcohol. A decided reaction for cineol was obtained, but none for phellandrene[3]).

547. Oil of Eucalyptus hemilampra.

Eucalyptus hemilampra, F. v. M. *(E. resinifera,* Sm. var. *grandiflora,* Benth.), a species that occurs in New South Wales, yields 0.375 p.c. of crude oil, for which Baker and Smith[4]) determined the following constants: d_{15}. 0.9282; $[\alpha]_D + 7.64°$; n_{D16}. 1.4735[2]); S. V. 24.37; soluble in 1.5 vol. of 70 p.c. alcohol. This oil contains much *cineol,* also *pinene, aromadendrene* and *aldehydes,* but no phellandrene.

548. Oil of Eucalyptus quadrangulata.

The occurrence of grey box, *Eucalyptus quadrangulata,* Deane et Maiden, is restricted to several localities in the neighborhood of Sydney. Baker and Smith[5]) obtained 0.684 p.c. of crude oil of an orange-red color which consisted almost entirely of d-*pinene* and *cineol* and which was free of phellandrene. d_{15}. 0.9064; $[\alpha]_D + 11.8°$; n_{D16}. 1.4692[2]); A.V. 1.0; E.V. 3.89; soluble in 2 vol. of 70 p.c. alcohol.

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[1]) Research, p. 56. — Bericht von Schimmel & Co. April 1888, 19; Report of Schimmel & Co. April 1904, 96. — Maiden, A critical revision of the genus Eucalyptus, vol. I, p. 261.

[2]) Smith, *loc. cit.* 45.

[3]) Report of Schimmel & Co. April 1904, 96.

[4]) Research, p. 57.

[5]) *Ibidem,* p. 58.

549. Oil of Eucalyptus conica.

Another box is the *Eucalyptus conica,* Deane et Maiden, which occurs west of the Dividing Range. Baker and Smith[1]) report the following data concerning its oil: — yield 0.587 p.c.; d_{15} 0.9057; $[\alpha]_D$ $+5.79°$; $n_{D16°}$ 1.4733[2]); A.V. 2; E.V. 4.26; soluble in 6 vol. of 70 p.c. alcohol. The oil contains *pinene* and *cineol* and probably a little *aromadrendral,* but no phellandrene. The rectified oil contain 40 p.c. *cineol.*

550. Oil of Eucalyptus Bosistoana.

Eucalyptus Bosistoana, F. v. M., known as ribbon or bastard box, is distributed over New South Wales and Victoria. Baker and Smith[3]) obtained 0.968 p.c. of an orange-red crude oil; $d_{15°}$ 0.9078; $[\alpha]_D$ $+10.2°$; $n_{D16°}$ 1.4732[2]); A.V. 2.6; E.V. 0.6; soluble in 5 vol. of 70 p.c. alcohol. The oil consists principally of *cineol, pinene* and *aromadendrene* and is free of phellandrene.

551. Oil of Eucalyptus eugenioides.

A white stringybark, *Eucalyptus eugenioides,* Sieb., occurs widely distributed over Victoria, New South Wales and Queensland. According to Baker and Smith[4]) the oil, yield 0.689 and 0.795 p.c. respectively, is almost colorless; $d_{15°}$ 0.9132 and 0.9122; $[\alpha]_D$ $+3.74$ and $5.246°$; $n_{D16°}$ 1.4747[2]); S.V. 6.89; the one oil soluble in 1.5 vol. of 70 p.c. alcohol, the other in an equal volume of 80 p.c. alcohol. In addition to 28 to 31 p.c. *cineol,* the oil contains *pinene,* but no phellandrene. Baker and Smith have observed that the cineol content of this oil, like that of other eucalyptus oils, increases upon standing, a phenomenon which they attribute to oxidation. The oil which originally contained 28 p.c. of cineol, after storage for $3^{1}/_{2}$ years, contained 62 p.c. The oil that had

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[1]) Research, p. 60.

[2]) Smith, *loc. cit.* 45.

[3]) Research, p. 61. — Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 1.

[4]) Journ. and Proceed. Royal Soc. of N. S. W. 32 (1898), 106; Report of Schimmel & Co. April 1899, 24. — Research, p. 62. See also Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 232.

been stored in a dark place had a density of 0.9171 at 15°, that exposed to light a density of 0.9202 at 15°.

552. Oil of Eucalyptus paniculata.

White ironbark, *Eucalyptus paniculata,* Sm., occurs in South Australia, Victoria, New South Wales, and Queensland. According to Baker and Smith[1]) the olive-brown oil, yield 0.104 p.c., has the following properties: $d_{15°}$ 0.901; $[\alpha]_D + 8.65°$; $n_{D16°}$ 1.4801[2]); A.V. 0.78; E.V. 6.33; S.V. after acetylation 56.14; soluble in an equal volume of 80 p.c. alcohol. In addition to much *pinene,* the oil contains little *cineol, aromadendrene, aromadendral,* also an *alcohol* not yet characterized.

553. Oil of Eucalyptus Seeana.

To this group there possibly also belongs the oil of *Eucalyptus Seeana,* Maiden, for which Smith[3]) records the following properties: $d_{16'}$ 0.9146; n_{D16} 1,4706; soluble in 1.4 vol. of 70 p.c. alcohol.

554. Oil of Eucalyptus acervula.

Eucalyptus acervula, Hook. f. occurs in Tasmania, where it is known as red gum of Tasmania. Baker and Smith[4]) distilled the oil with a yield of 0.212 p.c. and recorded the following properties for the crude oil: $d_{15°}$ 0.8956 and 0.898; $\alpha_D - 1.1°$; $n_{D18'}$ 1.4756; $n_{D22°}$ 1.4715; S.V. 32.8 and 34.3; S.V. after acetylation 105.3; soluble in an equal volume of 80 p.c. alcohol, upon addition of more alcohol the solution became turbid with the separation of paraffin. The oil contains as principal constituents d-*α-pinene* (nitrosochloride), also 21 p.c. of *cineol,* little *phellandrene, geranyl acetate,* free *geraniol,* a small amount of an *alcohol* not yet identified, also a *solid* (m.p. 55 to 56°) and a *liquid paraffin.*

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[1]) Research, p. 64. See also Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 104.

[2]) Smith, *loc. cit.* 46.

[3]) *Loc. cit.* 45.

[4]) A research on the eucalypts of Tasmania, Hobart 1912, p. 10; Report of Schimmel & Co. October 1918, 54.

Group IIIa.

Phellandrene-free oils consisting principally of cineol and pinene, the cineol content of which exceeds 40 p.c.

555. Oil of Eucalyptus resinifera.

Known as red or forest mahogany, *Eucalyptus resinifera*, Sm. occurs in the coast districts of New South Wales and Queensland. According to J. H. Gladstone [1]) the oil consists principally of a hydrocarbon that has the odor of turpentine oil. An oil distilled by Baker and Smith [2]) with a yield of 0.414 p.c. had the following properties: d_{15} 0.9098; $[\alpha]_D + 2.47^\circ$; n_{D16° 1.4755 [3]); S. V. 9.2; soluble in $1^3/_4$ vol. of 70 p.c. alcohol. The oil contains much cineol but no phellandrene. For an oil obtained from southern Australia, Schimmel & Co. [4]) report the following constants: d_{15} 0.9123; $\alpha_D + 6^\circ 1'$; and for an oil obtained from the Technological Museum in Sydney: d_{15° 0.9180; $\alpha_D + 2^\circ 5'$; with 10 vol. of 70 p.c. alcohol it did not yield a clear solution. It contained much *cineol* and no phellandrene.

A Portuguese oil, presumably from *Eucalyptus resinifera*, had a specific gravity of 0.893 and $\alpha_D - 17^\circ 8'$. It was not soluble in either 70 or 80 p.c. alcohol and contained *cineol* (iodol reaction) also *phellandrene* [5]).

556. Oil of Eucalyptus polyanthema.

Eucalyptus polyanthema, Schau., or red box, is a native of New South Wales and Victoria. From the leaves Baker and Smith [6]) obtained 0.825 p.c. of an amber-yellow oil for which they determined the following constants: d_{15° 0.9281; $[\alpha]_D + 5.8^\circ$; n_{D16° 1.4736 [7]); S. V. 20.7; soluble in $1^1/_4$ to 2 vol. of 70 p.c. alcohol. *Cineol* is the dominant constituent. *Pinene* is also present, but not phellandrene.

[1]) Journ. chem. Soc. 17 (1864), 1; Jahresber. d. Chem. 1863, 548.
[2]) Research, p. 67.
[3]) Smith, *loc. cit.* 45.
[4]) Report of Schimmel & Co. April 1904, 9b.
[5]) *Ibidem* October 1898, 26.
[6]) Research, p. 68. See also Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 109. As species name Maiden uses *polyanthemos*.
[7]) Smith, *loc. cit.* 44.

557. Oil of Eucalyptus Behriana.

One of the species occurring in the Mallee district[1]) of New South Wales, South Australia and Victoria is the *Eucalyptus Behriana*, F. v. M.   According to Baker and Smith[2]) the yield of oil amounts to 0.614 p.c.; $d_{15°}$ 0.9237; $[\alpha]_D + 4°$; $n_{D16°}$ 1.4765[3]); A. V. 2.3; E. V. 8.8; yields a clear solution with $1\frac{1}{2}$ vol. of 70 p.c. alcohol.   The crude oil contains large amounts of *cineol*, some *pinene*, but no phellandrene.

558. Oil of Eucalyptus Rossii.

White gum, *Eucalyptus Rossii*, Baker and Smith (*E. micrantha*, D. C.) occurs on the plateaus and in the coast regions of eastern Australia.   Baker and Smith[4]) obtained 0.719 p.c. of volatile oil, which was of a dark amber-yellow color and possessed an odor of peppermint: $d_{15°}$ 0.9215 and 0.9168; $[\alpha]_D + 7.8$ and $+ 7.9°$; $n_{D16°}$ 1.4741[5]); A. V. 2.9; E. V. 5.05; soluble in $1\frac{1}{4}$ to 1.5 vol. of 70 p.c. alcohol.   It was fairly rich in *cineol* and also contained *pinene* and a high boiling strongly dextrogyrate constituent.

559. Oil of Eucalyptus pendula.

Eucalyptus pendula, A. Cunn. (*E. largiflorens*, F. v. M.) is distributed over a large part of New South Wales and also occurs in South Australia, Queensland and northern Australia, where it is known as red box, also as *goborro*.   Baker and Smith obtained 0.843 p.c. of volatile oil: $d_{15°}$ 0.9155; $[\alpha]_D + 6°$; $n_{D16°}$ 1.4732[6]); A. V. 1.8; E. V. 6.6; soluble in 1,5 to 2 vol. of 70 p.c. alcohol.   The *cineol*-content amounted to 49 p.c.   Of hydrocarbons, *pinene* and *aromadendrene* were found, phellandrene was absent.

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[1]) The term Mallees is used not only to designate the shrubby eucalypts, but also the semi-arid regions covered by diverse low shrubs.

[2]) Research, p. 69.   See also Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 335.

[3]) Smith, *loc. cit.* 45.

[4]) Research, p. 70.

[5]) *Ibidem*, p. 71.

[6]) Smith, *loc. cit.* 44.

560. Oil of Eucalyptus dealbata.

Eucalyptus dealbata, A. Cunn., commonly known as cabbage, white gum, or mountain gum, occurs in numerous places of New South Wales and Queensland and yields 0.857 p.c. of oil. According to Baker and Smith[1]), it is one of the best cineol oils. The olive-oil-colored distillate had a density of 0.9261 (15°); $[\alpha]_D + 4.1°$; $n_{D16°} 1.4705$[2]); A.V. 1.1; E.V. 0.95; soluble in $1^1/_4$ vol. of 70 p.c. alcohol. *Cineol* was the predominant constituent. In addition it contains *pinene* and *aromadendrene*, but no phellandrene.

The oil with balm-like odor described on p. 537 of the first edition of this text-book as having been derived from *Eucalyptus dealbata*, no doubt, was obtained from a different species. It is very different in composition from the distillate described by Baker and Smith.

561. Oil of Eucalyptus tereticornis var. linearis.

From the leaves of *Eucalyptus tereticornis*, Sm., var. *linearis* Baker et Smith, which occurs in the northernmost districts of New South Wales, Baker and Smith[3]) obtained 0.783 p.c. of oil; $d_{15°} 0.91$; $[\alpha]_D + 6.15°$; A.V. 2.01; E.V. 3.48; soluble in $1^1/_4$ vol. of 70 p.c. alcohol. In addition to *cineol*, the principal constituent, the oil contains *pinene* and a very small amount of *sesquiterpene*.

562. Oil of Eucalyptus rostrata var. borealis.

According to Baker and Smith[4]), the leaves of *Eucalyptus rostrata*, Schl., var. *borealis* Baker et Smith, which grows along the Murray river and is known as river red gum, yield 0.795 to 1.191 p.c. of oil; $d_{15°} 0.9109$ and 0.9065; $[\alpha]_D + 5.99°$; $n_{D16°} 1.4747$[5]); S.V. 4.8 and 8; soluble in $1^3/_4$ vol. of 70 p.c. alcohol. The principal constituent is *cineol;* it also contains *pinene*.

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[1]) Research, p. 73.
[2]) Smith, *loc. cit.* 44.
[3]) Research, p. 74.
[4]) *Ibidem*, p. 75.
[5]) Smith, *loc. cit.* 45.

563. Oil of Eucalyptus maculosa.

Eucalyptus maculosa, R. T. Baker, spotted gum, or brittle gum, grows in a few districts of New South Wales. From the leaves Baker and Smith[1]) obtained 1.061 p.c. of oil: $d_{15°}$ 0.9158 and 0.9229; $[\alpha]_D + 3.66$ and $+ 2.49°$; $n_{D16°}$ 1.4741[2]); S. V. 21.3; soluble in $1^3/_4$ vol. of 70 p.c. alcohol. The oil contains as much as 50 p.c. of *cineol,* also d-*pinene,* a small amount of *aromadendrene* and probably a high boiling ester or alcohol.

564. Oil of Eucalyptus camphora.

The sallow or swamp gum, *Eucalyptus camphora,* R.T. Baker, grows in moist places of New South Wales, also in Victoria. The oil was described by Baker[3]), later by Baker and Smith[4]). Yield and composition vary with the season. In February the leaves yielded 1.34 p.c. of an amber-yellow oil ($d_{15°}$ 0.9071; $[\alpha]_D + 1.4°$; $n_{D16°}$ 1.4733[5]); A.V. 2.9; E.V. 1.5; soluble in $1^1/_2$ vol. of 70 p.c. alcohol) which contained about 50 p.c. of *cineol,* also *pinene* and *eudesmol.* An oil distilled in September with a yield of 0.398 p.c. ($d_{15°}$ 0.9167) contained much less cineol, but about 18 p.c. eudesmol, which distilled between 276 and 290° and solidified in the receiver. Both distillates were free from phellandrene.

565. Oil of Eucalyptus punctata.

Eucalyptus punctata, D. C.[6]), known in Australia as grey gum, yields a very hard wood as well as kino. It is found along the entire coast from Queensland to the border of Victoria.

In the production of the oil Baker and Smith[7]) used leaves and young branches. Nine different distillations of material

[1]) Research, p. 76. — Baker, Proceed. Linnean Soc. of N. S. W. 1899, 598; Report of Schimmel & Co. October 1900, 33.

[2]) Smith, *loc. cit.* 44.

[3]) Proceed. Linnean Soc. of N. S. W. 1899, 292; Report of Schimmel & Co. April 1900, 27.

[4]) Research, p. 78, 212.

[5]) Smith, *loc. cit.* 45.

[6]) Maiden (*loc. cit.* 506) mentions as synonymous for this species: *Eucalyptus tereticornis,* var. *brachycorys,* Benth.; Baker and Smith do not do so.

[7]) Journ. and Proceed. Royal Soc. of N. S. W. 31 (1897), 259; Report of Schimmel & Co. October 1898, 27. — Research, p. 80.

from various districts were made. The yield varied between 0.63 and 1.19 p. c. The specific gravity fluctuated between 0.9129 and 0.9297 at 15°. Two oils were lævogyrate ($[\alpha]_D$ — 0.92 and — 2.52°), the remaining seven dextrogyrate ($[\alpha]_D$ + 0.54 to + 4.44°). An average sample of all distillates had the following properties: $d_{15°}$ 0.927 [1]); $n_{D16°}$ 1.4774 [2]); the cineol content, determined according to the phosphoric acid method, amounted to between 46.4 and 64.5 p. c. Phellandrene was not present in the oil, but *aromadendral* presumably was [1]).

In connection with a commercial product Schimmel & Co. observed the following properties: $d_{15°}$ 0.9060; α_D + 4° 10′; soluble in 1 to 1.5 vol. and more of 80 p. c. alcohol, insoluble in 10 vol. of 70 p. c. alcohol. The oil gave a strong test for *cineol* but none for phellandrene, and contained small amounts of *cuminic aldehyde* [3]).

566. Oil of Eucalyptus squamosa.

The oil of *Eucalyptus squamosa* Deane et Maiden, ironwood, a tree growing in Cumberland County, New South Wales, according to Baker and Smith [4]), is a faintly colored product of which 0.644 p. c. is obtained from the leaves: $d_{15°}$ 0.9182; $[\alpha]_D$ + 0°; n_{D16} 1.4692 [5]); A. V. 0.81; S. V. 4.65; soluble in $1^{1}/_4$ vol. of 70 p. c. alcohol. The oil contains 60 p. c. *cineol*, also small amounts of *pinene* and *aromadendral*, and occasionally *phellandrene*.

567. Oil of Eucalyptus Bridgesiana.

Eucalyptus Bridgesiana, R. T. Baker grows in New South Wales and Victoria where it is known as apple, woolly-butt, or butt-butt of Gippsland. The oil contains a high percentage of *cineol*, but its yield is small, hence this species is not used for the production of oil. Baker and Smith [6]) obtained yields varying

[1]) Journ. and Proceed. Royal Soc. of N. S. W. 31 (1897), 259; Report of Schimmel & Co. October 1898, 27. — Research, p. 80.

[2]) Smith, *loc. cit.* 45.

[3]) Report of Schimmel & Co. April 1904, 96.

[4]) Research, p. 48. See also Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 221.

[5]) Smith, *loc. cit.* 44.

[6]) Research p. 86. — Journ. and Proceed. Royal Soc. of N. S. W. 45 (1911), 276; Report of Schimmel & Co. October 1912, 63.

from 0.571 to 0.75 p. c. from the leaves: $d_{15°}$ 0.912 to 0.9246; $a_D + 1.8$ to $[a]_D + 3.67°$; $n_{D20'}$ 1.4716 to 1.4729; A.V. 2.3; E.V. 3.9; soluble in $1^1/_2$ vol. of 70 p. c. alcohol. The crude oil is rich in cineol containing as much as 73 to 78 p. c. (determined according to the phosphoric acid method). Other constituents are *α-pinene* (characterized by the usual reactions) and *aromadendrene.* Phellandrene was not found.

568. Oil of Eucalyptus goniocalyx.

The oil of *Eucalyptus goniocalyx* F. v. M.[1]), one of the species known as mountain gum, was mentioned by Wilkinson[2]) and Maiden[3]) many years ago. Baker and Smith[4]) describe the oil (yield 0.959 p.c.) as a liquid of light lemon-yellow color; $d_{15°}$ 0.9117 and 0.9125; $[a]_D + 4.77$ and 7.89°; $n_{D16°}$ 1.4746[5]); A.V. 3.8; E.V 9.5; soluble in $1^1/_4$ to $1^1/_2$ vol. of 70 p. c. alcohol. The oil contained about 55 p. c. *cineol,* also *α-pinene* (characterized by the customary reactions), *eudesmol, valeric* and *acetic acid* esters, but no phellandrene. Upon standing a white pulverulent substance separates from the oil (comp. *Eucalyptus gracilis,* p. 261).

For an oil obtained from the Technological Museum of Sydney Schimmel & Co.[6]) found: $d_{15°}$ 0.9163; $a_D + 5° 2'$; insoluble in 10 vol. of 70 p. c. alcohol, soluble in 1.2 vol. and more of 80 p. c. alcohol. It yielded a moderately strong reaction for *phellandrene.*

According to Maiden[3]) this oil has the following properties: d 0.918 to 0.920; $[a]_D - 4.3°$[2]); b. p. 152 to 175°.

569. Oil of Eucalyptus bicolor.

According to Baker and Smith[7]) the leaves of *Eucalyptus bicolor,* A. Cunn., bastard box, which is native to New South

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[1]) See Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 267.
[2]) Proceed. Royal Soc. of Victoria 1898, 198.
[3]) Useful native plants of Australia. London and Sydney 1889, p. 268.
[4]) Research, p. 88.
[5]) Smith, *loc. cit.* 45.
[6]) Observations from the laboratory of Schimmel & Co.
[7]) Research, p. 90. See also Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 6.

Wales, yield 0.520 p.c. of oil, which in the crude condition is amber-colored: $d_{15°}$ 0.9259; $[\alpha]_D + 1.2°$; $n_{D16°}$ 1.4734[1]); A.V. 1.06; E.V. 2.54; soluble in $1^1/_4$ vol. of 70 p.c. alcohol. It consists principally of *cineol* and a *sesquiterpene*.

An oil described many years ago by Schimmel & Co.[2]) (d 0.8866; $\alpha_D — 21°50'$) was most likely not derived from this species. It contained much *phellandrene* and little *cineol*.

570. Oil of Eucalyptus viminalis var. a.

Eucalyptus viminalis var. *a*, which occurs in the Crookwell district of New South Wales, yields 0.7 p.c. of an amber-colored oil with an odor reminding of benzaldehyde[3]); $d_{15°}$ 0.9122; $[\alpha]_D + 7.34°$; $n_{D16°}$ 1.4711[4]); A.V. 0.6; E.V. 4.07; soluble in 1.5 vol. of 70 p.c. alcohol. *Cineol* is the principal constituent. *Pinene* is likewise present but the test for phellandrene gave a negative result.

When shaken with bisulphite solution, the oil yielded a small amount of a solid compound, but it was impossible to identify benzaldehyde.

571. Oil of Eucalyptus populifolia.

Eucalyptus populifolia, Hook., bembil box or poplar-leaved box, is a native of New South Wales, Queensland and northern Australia. Baker and Smith[5]) obtained 0.661 and 0.856 p.c. of a light yellowish-brown oil: $d_{15°}$ 0.920 and 0.923; $[\alpha]_D + 0.43$ and $+1.3°$; $n_{D16°}$1.4709[1]); A.V. 1.9; soluble in $1^1/_4$ vol. of 70 p.c. alcohol. *Cineol* is present to the extent of 57 to 62 p.c., *pinene* and a *sesquiterpene* in subordinate amounts. Upon standing a precipitate is formed, as is the case with other eucalyptus oils (see p. 261). According to Schimmel &,Co.[6]) the oil contains *cuminic aldehyde* and relatively much cineol.

[1]) Smith, *loc. cit.* 44.

[2]) Report of Schimmel & Co. October 1900, 32.

[3]) Research, p. 91.

[4]) Smith, *loc. cit.* 45.

[5]) Research, p. 92. See also Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 339.

[6]) Report of Schimmel & Co. April 1898, 38.

572. Oil of Eucalyptus longifolia.

The oil of *Eucalyptus longifolia,* Link et Otto (*E. Woollsii,*
F. v. M.[1])), woolly butt, was mentioned by Maiden[2]) some years
ago. Later it was examined more fully by Baker and Smith[3]).
This species is a native of New South Wales and Victoria.
Its leaves yield 0.535 p. c. of oil: $d_{15°}$ 0.9226; $[\alpha]_D + 3.1°$;
$n_{D16°}$ 1.4738[4]); A.V. 2.2; E.V. 1.4; soluble in $1^{1}/_2$ vol. of 70 p. c.
alcohol. This oil contains much *cineol* little *pinene* and a *sesqui-
terpene*. According to Maiden[2]) the oil is viscid, has an aromatic,
cooling taste and a camphor-like odor; b. p. 194 to 215°; d 0.940.

573. Oil of Eucalyptus Maideni.

One of the blue gums, the *Eucalyptus Maideni,* F. v. M., is
a native of the north of New South Wales. From the leaves
Baker and Smith[5]) obtained 1 p.c. of an oil; $d_{15°}$ 0.9247; $[\alpha]_D + 5.3°$;
$n_{D16°}$ 1.4736[6]); S.V. 21.8. It was rich in *cineol* and also contained
pinene and *sesquiterpene*.

574. Oil of Eucalyptus Globulus.

Origin. Of all of the eucalypts, *Eucalyptus Globulus,* Lab.
is best known outside of Australia and most highly esteemed[7]).
The beneficial influence which its cultivation exerts in making
malarial regions more sanitary is, no doubt, attributable to the
drying up of marshes rather than to any balsamic emanation
of its leaves. Formerly it was supposed that the transpiration
of the leaves must be great since the trees dried up swamps
so readily. However, the error of this assumption was demon-

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[1]) Comp. Maiden, A critical revision of the genus Eucalyptus, vol. II p. 295.
[2]) Useful native plants of Australia, p. 270.
[3]) Research, p. 94.
[4]) Smith, *loc. cit.* 45.
[5]) Research, p. 95. See also Maiden, A critical revision of the genus
Eucalyptus, vol. II. p. 256.
[6]) Smith, *loc. cit.* 44.
[7]) According to A. F. Collins (Chemist and Druggist 67 [1905], 103), the
oils of *Eucalyptus dumosa* and *E. oleosa* are sold as globulus oils and not
the oils labled as globulus oils in the market are actually derived
from *Eucalyptus Globulus.*

strated by E. Griffon [1]) who showed that the transpiration capacity of willow, birch and ash is two to three times as great as that of the eucalyptus leaves. Hence the drying capacity of the eucalyptus is attributable to its capacity to produce a large foliage surface in a very short time [2]).

This species, known in Australia as blue gum, requires about the same climatic conditions as does the orange tree. Its excellent qualities caused it to be transplanted to all parts of the globe. It is now found in Algiers, southern France, Italy, Spain and Portugal, California, Florida, Mexico, Jamaica, Transvaal, India and numerous other countries. In Australia it is found principally in Tasmania, but it also occurs in the southwestern part of this continent. In their large monograph on the eucalypts [3]) Baker and Smith further mention its occurrence about Nullo mountain and Jenolan caves (New South Wales), also in Victoria.

According to F. von Müller the fresh leaves yield 0.71 p.c. of oil. From the dried leaves Schimmel & Co. obtained yields varying from 1.6 to 3 p.c.

Properties. Oil of *Eucalyptus Globulus* is a very mobile liquid which is either colorless or possesses a light yellow color, an agreeable refreshing cineol odor and a spicy, cooling taste. In the case of crude oils the presence of aldehydes, particularly valeric aldehyde, manifests itself by an irritating action producing coughing. Well-rectified oils do not possess this property, or at least in a slight degree only. For commercial oils designated globulus oils Schimmel & Co. determined the following properties: $d_{15°}$ 0.910 to 0.930; α_i, dextrogyrate up to $+15°$; $n_{D20°}$ 1.460 to 1.469; soluble in 2 to 3 vol. and more of 70 p.c. alcohol. Crude oils are, occasionally, not as readily soluble. For crude oils Baker and Smith [4]) record the following properties: $d_{15°}$ 0.913; $[\alpha]_D +9.2°$; $n_{D18°}$ 1.470 [5]); A.V. 1.1; E.V. 1; soluble in 1.5 vol. of 70 p.c. alcohol.

[1]) Compt. rend. 188 (1904), 157.

[2]) See also A. Zimmermann, Der Pflanzer 9 (1913), 107.

[3]) Research, p. 97. See also: Baker and Smith, A research on the eucalypts of Tasmania, Hobart 1912, p. 16. — Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 249.

[4]) Research, p. 96.

[5]) Smith, *loc. cit.* 44.

· The density of the oil increases with the cineol (eucalyptol) content whereas the angle of rotation diminishes. Oils with a high eucalyptol content congeal to a white crystalline mass when exposed to the temperature of a freezing mixture of ice and salt.

· **Composition.** Eucalyptus oil was first investigated by Cloez[1] in 1870. By means of fractional distillation he separated a substance boiling at 175° which he named eucalyptol. From the low specific gravity (0.905 instead of 0.930), also from the optical rotation of the fraction, it becomes apparent that it was still largely contaminated with terpenes, for which reason the elementary analysis yielded Cloez the wrong empirical formula, viz. $C_{12}H_{22}O$.

Several years later (1874) A. Faust and J. Homeyer[2] examined an eucalyptus oil concerning the origin of which they make no statement. The fact that fraction 171 to 174° of this oil contained no oxygen proves that the oil could not have been that of *Eucalyptus Globulus*.

The correct composition of eucalyptol as $C_{10}H_{18}O$ was recognized by E. Jahns[3] who proved its identity with *cineol*. He availed himself of the method of O. Wallach and W. Brass[4] to isolate the pure cineol by passing hydrogen chloride into the fraction. For the properties of cineol see vol. I, p. 526.

·The hydrocarbon accompanying cineol, formerly known as eucalyptene, is nothing more or less than d-α-*pinene*. By passing dry hydrogen chloride into fraction 165°), O. Wallach and E. Gildemeister[5] obtained solid pinene monohydrochloride. With amyl nitrite and hydrochloric acid a nitrosochloride resulted which, when boiled with alcoholic potassa, yielded nitrosopinene (m. p. 129 to 130°); likewise, when heated with piperidine, yielded pinene nitrol piperidine melting at 116°.

Other observations render it probable that in addition to α-pinene globulus oil contains other terpenes. When treating

[1] Compt. rend. 70 (1870), 687. — Liebig's Annalen 154 (1870), 372.

[2] Berl. Berichte 7 (1874), 63.

[3] Berl. Berichte 17 (1884), 2941. — Arch. der Pharm. 223 (1885), 52.

[4] Liebig's Annalen 225 (1884), 291.

[5] *Ibidem* 246 (1888), 283. — Comp. also Voiry, Bull. Soc. chim. II. 50 (1888), 106.

Fig. 20. Flowering branch of *Eucalyptus Globulus*.

fraction 156 to 157' with formic acid, Bouchardat and Tardy[1]) obtained terpineol, *iso*borneol and fenchyl alcohol. The formation of terpineol is explained by the presence of pinene, whereas the formation of *iso*borneol and fenchylalcohol may be attributed to camphene and fenchene. The observations of Bouchardat and Tardy have been largely verified by Schimmel & Co.[2]); however, upon heating the terpene fraction boiling at 155° with benzoic acid to 150' they could not obtain fenchyl alcohol. In the same fraction the presence of camphene could readily be proven.

The unpleasant odor of crude eucalyptus oil which produces coughing is due to various aldehydes, more particularly *valeric aldehyde,* also *butyric* and *capronic aldehydes*[2]). According to G. Bouchardat and Oliviero[3]) the first fractions also contain *ethyl* and *amyl alcohol.* In addition Wallach and Gildemeister[4]) found fatty acids the nature of which has not been determined. The amyl alcohol isolated by Schimmel & Co.[2]), after having been purified by means of its calcium chloride addition product, boiled at 131° and yielded a phenylurethane (m.p. 52 to 53°) which when mixed with that of technical *iso*amyl alcohol suffered no melting point depression. It thus became apparent that the oil contains iso*amyl alcohol.* After freeing the fraction boiling near 140' from terpenes, by oxidation in the cold, with potassium permanganate, Schimmel & Co. obtained a residual oil that had the characteristic odor of amyl acetate.

The portions of the oil that boil above 200° are lævogyrate and in the course of the distillation yield an acid (acetic acid?), hence they contain an ester. Upon saponification an alcohol boiling between 215 and 220° is obtained. As shown by Wallach[5]) there can be but little doubt that this alcohol is the optically active modification of *pinocarveol* prepared synthetically by him[6]). The alcohol, purified by means of its acid phthalic ester (action of phthalic acid anhydride on the sodium compound of the alcohol in ethereal solution) revealed the following constants: b.p.92°(12mm);

[1]) Compt. ▓▓▓▓ 895), 1417.
[2]) Report ▓▓▓▓ & Co. April 1904, 53.
[3]) Bull. ▓▓▓▓ III. 9 (1893), 429.
[4]) Loc.
[5]) Lieb ▓▓▓ alen 346 (1906), 227
[6]) Ibi ▓▓ 1.

d 0.9745; $[\alpha]_D$ — 52.45° (in 12.75 p.c. solution); n_{D20_0} 1.49630. The analysis left no doubt that the substance had the formula $C_{10}H_{15}OH$. The phenylurethane was resolved into two parts, one of which melted at 94 to 95°, the other at 82 to 84°. Upon oxidation the alcohol yielded a ketone $C_{10}H_{14}O$ which yielded two semicarbazones (m.p. 209 to 210° and above 300). The semicarbazone of the melting point 209 to 210° was the principal product. Whereas the free ketone $C_{10}H_{14}O$ bore the greatest resemblance to pinocarvone, its oxime boiled at 140° (20 mm.) and upon cooling congealed to a crystalline mass which revealed a melting point much lower than that of pinocarvoxime. Possibly the differences are due to the fact that one of the oximes is active and the other inactive.

In the highest fraction of an oil Schimmel & Co.[1] observed crystals which, after being freed from adhering oil by pressing on porous plates and recrystallization from 70 p.c. alcohol, were obtained as shiny, almost odorless needles melting at 88.5°. b.p. 283° (755 mm); $[\alpha]_D$ — 35° 29′ (12 p.c. chloroform solution). Elementary analysis gave figures in agreement with the formula for a sesquiterpene alcohol $C_{15}H_{25}OH$. An attempt was made to convert the alcohol into its ester by acetylation. However, only about 5 p.c. of ester was obtained, whereas most of the alcohol had been dehydrated to hydrocarbon. Dehydration is best accomplished by means of 90 p.c. formic acid when a mixture of dextro- and lævogyrate hydrocarbons results. After frequently repeated fractionations a separation of two isomeric sesquiterpenes resulted which, after treatment with aqueous alkali and distillation over metallic sodium, revealed the following constants: I. (l-sesquiterpene) b. p. 102 to 103° (6 mm), 247 to 248°; (748 mm) d_{15} 0.8956; α_D — 55°48′; $n_{D20°}$ 1.49287. II. (d-sesquiterpene) b.p. 265.5 to 266° (750 mm.); d_{15} 0.9236; α_D + 58° 40′; $n_{D20°}$ 1.50602.

Other dehydrating agents, such as sulphuric acid and phosphorus pentoxide, yielded both hydrocarbons though in varying proportions.

Neither the sesquiterpene alcohol nor the hydrocarbons derived therefrom agree, as to physical properties, with any of their known isomers.

[1] Report of Schimmel & Co. April 1904, 51.

For the alcohol F. W. Semmler and E. Tobias[1]) suggest the name *globulol*. In their opinion it is different physically, and possibly also chemically, from eudesmol. It is not excluded, however, that similar relations may exist between eudesmol and globulol as between borneol and *iso*borneol.

In an oil distilled by themselves Baker and Smith[2]) (comp. p. 245) found *eudesmol* and a *sesquiterpene* in addition to *pinene*. The sesquiterpene produces the red color which results upon the treatment of the oil with phosphoric acid.

575. Oil of Eucalyptus pulverulenta.

Eucalyptus pulverulenta, Sims. (*E. pulvigera*, A. Cunn.)[3]) is one of the shrubby species and its occurrence is restricted to a few places in New South Wales. From the leaves Baker and Smith[4]) obtained 2.22 p.c. of an amber-colored oil: d_{15} 0.9236; $[\alpha]_D + 2.3°$; $n_{D16°}$ 1.4686[5]); A.V. 1.38; E.V. 16.98; soluble in $1^1/_4$ vol. of 70 p.c. alcohol. It is rich in *cineol* and contains *pinene*, but no phellandrene.

Schimmel & Co.[6]) found the following properties: d_{15} 0.9217; $\alpha_D + 1°4'$; soluble in 2 vol. of 70 p.c. alcohol. The oil contained much cineol but gave a very faint *phellandrene* reaction.

576. Oil of Eucalyptus cinerea.

Eucalyptus cinerea, F. v. M.[7]), the Argyle apple, is a native of New South Wales. According to Baker and Smith[8]) the leaves yield from 1 to 1.3 p.c. of oil which, when rectified, is of a yellow

[1]) Berl. Berichte 46 (1913), 2030.

[2]) Research, p. 96.

[3]) According to Maiden (A critical revision of the genus Eucalyptus, vol. III. p. 1) *E. pulverulenta*, F. v. M. non Sims. is synonymous with *E. cinerea*, F. v. M. On the other hand, *E. pulverulenta*, Sims. is synonymous with *E. rigida*, Hoffmg. and *E. cordata*, Lodd. non Lab.

[4]) Research, p. 98.

[5]) Smith, *loc. cit.* 44.

[6]) Report of Schimmel & Co. April 1902, 39.

[7]) See also Maiden, A critical revision of the genus Eucalyptus, vol. III. p. 1. According to this author *E. cinerea* is synonymous with *E. pulverulenta*, F. v. M., *E. Stuartiana secunda*, F. v. M., *E. pulverulenta*, F. v. M. var. *lanceolata*, Howitt and *E. Stuartiana* var. *cordata*, Baker and Smith.

[8]) Research, p. 100, 251.

color. The crude oil has the following properties: d_{15} 0.9113 to 0.9225; $[\alpha]_D + 2.7$ to $4.46°$; $n_{D16°}$ 1.4706[1]); A.V. 1.4; E.V. 14.4 to 22.6. It contains 59 % *cineol*, also *pinene* and relatively much ester. In the aqueous distillate Baker and Smith found *acetic acid*.

577. Oil of Eucalyptus Stuartiana.

Eucalyptus Stuartiana, F.v.M., known as apple of Victoria, is a native of that province. Its leaves yield 0.394 p.c. of oil; $d_{15°}$ 0.916; $[\alpha]_D + 5.24°$; $n_{D16°}$ 1.4790[2]); S.V. 14.2; soluble in $1^1/4$ vol. of 70 p.c. alcohol[3]). It contains 53 p.c. *cineol,* also *pinene* and an ester, but no phellandrene. According to Wilkinson[4]) the oil has the following properties: d 0.917 to 0.932; $[\alpha]_D - 7$ to $- 16°$.

578. Oil of Eucalyptus Stuartiana var. cordata.

Eucalyptus Stuartiana var. *cordata*, Baker et Smith[5]) (*E. pulverulenta* var. *lanceolata*, A. W. H.) is also a native of Victoria. According to Baker and Smith[6]) its oil closely resembles that of *E. cinerea*. The yield amounts to 1.13 p.c.: $d_{15°}$ 0.934; S.V. 35.2; soluble in $1^1/2$ vol. of 70 p.c. alcohol. It does not contain as much *cineol* as the preceding oil.

579. Oil of Eucalyptus Morrisii.

According to Baker and Smith[7]) the shrub-like *Eucalyptus Morrisii*, R.T. Baker, the grey mallee, which ●●●ws in stony soil, is suitable for production of oil of which it yielded 1.613 and 1.69 p.c. respectively: $d_{15°}$ 0.9097 and 0.9164; $[\alpha]_D + 4.1$ and $+ 6.7°$; $n_{D16°}$ 1.4693[1]); A.V. 2.4; E.V. 5.7; soluble in $1^1/2$ vol. of 70 p.c. alcohol. It contains from 58 to 63 p.c. of *cineol,* also d-*pinene* but no phellandrene.

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[1]) Smith, *loc. cit.* 44.

[2]) *Ibidem* 45.

[3]) Proceed. Royal Soc. of Victoria 1893, 198.

[4]) Research, p. 103.

[5]) According to Maiden, A critical revision of the genus Eucalyptus, vol. III. p. 1 this species is synonymous with *E. cinerea*, F. v. M.

[6]) Research, p. 105.

[7]) *Ibidem*, p. 105. — Baker, Proceed. Linnean Soc. of N. S. W. 1900, 312; Report of Schimmel & Co. October 1901, 28.

580. Oil of Eucalyptus Smithii.

One of the oils richest in cineol is that of *Eucalyptus Smithii*, R. T. Baker, known as white top, gully ash and white ironbark, which is native to New South Wales and possibly occurs in Victoria as well. Baker and Smith[1]) obtained 1.14 to 1.78 p.c. of a light reddish-yellow oil: $d_{15°}$ 0.915 to 0.9158; $[\alpha]_D + 5.35$ to $6.72°$; $n_{D16°}$ 1.4706[2]); A. V. 1.6; E. V. 0.8; soluble in $1\frac{1}{4}$ vol. of 70 p.c. alcohol. The *cineol* content amounts to about 70 p.c. Other constituents are d-*pinene* and little *eudesmol*. The oil from the "sucker leaves" (see p. 229) is practically identical with that from the old leaves. In the aqueous distillate Baker and Smith found *acetic acid* (barium salt).

In connection with oils secured from Australia, Schimmel & Co. observed the following constants: $d_{15°}$ 0.9166 to 0.9249; $\alpha_D + 0°24'$ to $+ 4°5'$; $n_{D20°}$ 1.46130; soluble in 1.5 to 3 vol. and more of 70 p.c. alcohol. As high as 80 p.c. of *cineol* were found. The phellandrene test gave negative or but faintly positive results.

581. Oil of Eucalyptus sideroxylon.

Eucalyptus sideroxylon, A. Cunn. (*E. Leucoxylon*, F. v. M. part.) known as red flowering ironbark, occurs in New South Wales and Victoria. The oil, yield 0.743 p.c., is described by Baker and Smith[3]) as a reddish-yellow liquid: $d_{15°}$ 0.9189 fo 0.9227; $[\alpha]_D + 1.52$ to ; $n_{D16°}$ 1.4725[2]); A. V. 1.1; E. V. 1.4; soluble in $1\frac{1}{4}$ vol. of 70 p.c. alcohol. It contains 57 to 60 p.c. *cineol*, pinene and a small amount of sesquiterpene and an aldehyde.

Whether the oils, reported earlier by Bosisto[4]) and by Wilkinson[5]) as being derived from *E. Leucoxylon*, were really obtained from *Eucalyptus sideroxylon* is uncertain.

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[1]) Research, pp. 107, 251. — Baker, Proceed. Linnean Soc. of N. S. W. 1899, 292; Report of Schimmel & Co. April 1900, 27. See also Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 76.

[2]) Smith, *loc. cit.* 44.

[3]) Research, p. 111. See also Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 82.

[4]) Maiden, The useful native plants of Australia, p. 270.

[5]) Proceed. Royal Soc. of Victoria, 1898, 198.

582. Oil of Eucalyptus salmonophloia.

To this group belongs also the oil of *Eucalyptus salmonophloia*, F. v. M., the salmon bark gum, a tree characteristic of western Australia[1]). Baker and Smith[2]) obtained a yield of 1.44 p.c.; $d_{15°}$ 0.9076; $\alpha_D + 6.3°$; $n_{D16°}$ 1.4738; E.V. 4.97; soluble in $3^1/_2$ vol. of 70 p.c. alcohol. The dominant constituents are *cineol* and *pinene*. It also contains *aromadendral*.

583. Oil of Eucalyptus cordata.

According to Baker and Smith[3]), the occurrence of *Eucalyptus cordata*, Labill.[4]) is restricted to Tasmania. The leaves yielded 2.32 p.c. of oil; d 0.9138; $\alpha_D + 9.3°$; $n_{D16°}$ 1.4695[5]); A.V. 2.76; E.V. 12.09; soluble in $1^1/_4$ vol. of 70 p.c. alcohol. The oil consists chiefly of *cineol*. It also contains *pinene*, but no phellandrene.

584. Oil of Eucalyptus Muelleri.

Judging from the composition of the oil, *Eucalyptus Muelleri*, T. B. Moore[6]) belongs to this group. This Tasmanian species is closely related to *Eucalyptus vernicosa* and is known as brown gum. The oil yield amounts to 1.28 p.c.; $d_{15°}$ 0.9096; $\alpha_D + 10.4°$; $n_{D24°}$ 1.4629; S.V. 15.3; soluble in 4 vol. of 70 p.c. alcohol. The oil contains 60 p.c. *cineol*, much *pinene*, also *geranyl acetate*, but no phellandrene.

585. Oil of Eucalyptus Perriniana.

To this same group there probably also belongs the oil of the Tasmanian *Eucalyptus Perriniana*, Baker et Smith, which

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[1]) See L. Diels, *Die Pflanzenwelt von Westaustralien*, Leipzig 1906, p. 266.

[2]) Pharmaceutical Journ. 75 (1905), 375; Report of Schimmel & Co. April 1906, 31. — See also Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 217.

[3]) Research, p. 209.

[4]) Comp. Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 282.

[5]) Smith, *loc. cit.* 44.

[6]) Baker and Smith, A research on the eucalypts of Tasmania, Hobart 1912, p. 23; Report of Schimmel & Co. October 1913, 57.

Baker and Smith[1]) distilled with a yield of 1 p.c.; d_{15° 0.9119; α_D + 8.9°; n_{D15° 1.4651; S.V. 10.3; soluble in twice its volume of 70 p.c. alcohol. The *cineol* content amounts to 68 p.c. In addition it contains much *pinene*, also a *sesquiterpene*.

586. Oil of Eucalyptus unialata.

Eucalyptus unialata, Baker et Smith *(E. viminalis* var. *macrocarpa)* is indigenous to Tasmania. Baker and Smith[2]) distilled the oil with a yield of 0.897 p.c.; d_{15° 0.9179; α_D + 3.1°; n_{D18° 1.4690; S.V. 11.1; soluble in $1^3/_4$ vol. of 70 p.c. alcohol; upon addition of 10 vol. the solution becomes turbid. Constituents: 62 p.c. *cineol* (resorcinol method), d-*pinene* and a *sesquiterpene*.

587. Oil of Eucalyptus urnigera.

Urn gum or *Eucalyptus urnigera*, Hook. f. yields 1.13 p.c.[3]) of oil: d_{15° 0.9088; α_D + 11.8°; n_{D28° 1.4638; S.V. 18.3; soluble in 5 vol. of 70 p.c. alcohol. It contains about 63 p.c. *cineol*, d-*pinene* and *geranyl acetate*.

588. Oil of Eucalyptus vernicosa.

Eucalyptus vernicosa, Hook. f. is a native of Tasmania. Baker and Smith[4]) obtained 0.807 p.c. of volatile oil; d_{15° 0.9038; α_D + 11.3°; n_{D18° 1.4651; S.V. 5.9; soluble in an equal volume of 80 p.c. alcohol. The oil contains 59 p.c. *cineol* and much d-*pinene*.

589. Oil of Eucalyptus Rodwayi.

The apple-scented gum or black gum, *Eucalyptus Rodwayi*, Baker et Smith, is a native of Tasmania[5]). It yields 0.482 p.c. of oil; d_{15° 0.9075; α_D + 10.6°; n_{D24° 1.4653; S.V. 3.96; soluble in 6 vol. of 70 p.c. alcohol. It contains more than 60 p.c. of *cineol* (resorcinol method) also d-α-*pinene* and a *sesquiterpene*.

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[1]) Baker and Smith, A research on the eucalypts of Tasmania, Hobart 1912, p. 25.
[2]) *Ibidem* 38.
[3]) *Ibidem* 40.
[4]) *Ibidem* 42.
[5]) *Ibidem* 53.

Group IIIb.

Oils containing more than 40 p.c. of cineol, which contain less pinene but in which aromadendral occurs.

590. Oil of Eucalyptus Cambagei.

In the central districts of New South Wales and Victoria is found the bundy or bastard box, *Eucalyptus Cambagei*, Deane et Maiden (*E. elæophora*, F. v. M.; *E. goniocalyx*, F. v. M. var. *pallens*, Benth.)[1]). According to Baker and Smith[2]) the leaves yield 0.829 to 0.835 p.c. of crude oil which is of a reddish, orange-brown color; d_{15° 0.9191 to 0.9208; $[\alpha]_D$ —0.75 to + 6.16°; n_{D16° 1.4720[3]); A. V. 3.4; E. V. 4.2 to 5.37. In addition to much *cineol* it contains *pinene, aromadendral* and *eudesmol*, but no phellandrene.

591. Oil of Eucalyptus polybractea.

Eucalyptus polybractea, R. T. Baker, blue mallee or silver mallee[4]), one of the mallee shrubs[5]) is a native of the interior of New South Wales. Together with *E. dumosa*, it constitutes the blue mallee of the whipstickscrubs of a desolate area in Bendigo (Victoria) covered with eucalypts. Here it is distilled on a large scale[6]). The light yellow oil is obtained, according to Baker and Smith[7]), with a yield of 1.35 p.c. During recent years it has been produced in Australia in large quantities[8]) and is said to be particularly suited for certain purposes[9]). It is very rich in *cineol*. *Pinene* and *aromadendral* were detected

[1]) See also Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 275.

[2]) Research, p. 113.

[3]) Smith, *loc. cit.* 44.

[4]) Perfum. Record 5 (1914), 22.

[5]) See p. 238.

[6]) Bendigo Advertiser of March 1913; Report of Schimmel & Co. October 1913, 54.

[7]) Research, p. 116. — Proceed. Linnean Soc. of N. S. W. 1900, 692; Report of Schimmel & Co. April 1902, 40.

[8]) Report of Schimmel & Co. October 1907, 45.

in small amounts only. $d_{15°}$ 0.9143; $[\alpha]_D$ — 2.13°; $n_{D15°}$ 1.4692 to 1.4736[1]); A.V. 0.99; E.V. 3.51; soluble in $1\frac{1}{2}$ vol. of 70 p.c. alcohol.

In connection with an oil obtained from the Technological Museum at Sydney, Schimmel & Co.[2]) determined the following constants: $d_{15°}$ 0.9193; α_D — 1°3′; $n_{D20°}$ 1.46743; not soluble in 10 vol. of 70 p.c. alcohol, soluble in an equal vol. of 80 p.c. alcohol, the addition of more solvent causes opalescence. The phellandrene reaction gave a negative result. In connection with commercial oils the same firm records the following observations: $d_{15°}$ 0.9282 to 0.9301; α_D + 0′10′ to + 0″41′; $n_{D20°}$ 1.45921 to 1.46111; soluble in 4 vol. of 60 p.c. and 1.6 to 2 vol. and more of 70 p.c. alcohol. The cineol content amounted to from 85 to 94 p.c. In one instance the congealing point was found at - 3.8°.

An oil of *Eucalyptus polybractea* examined by J. C. Umney and C. T. Bennett[3]) revealed d 0.929; $\alpha_D \pm 0$°; *cineol* content determined by the phosphoric acid method, 79 to 80 p.c. E. M. Holmes[4]) is of the opinion that this oil was no normal distillate. Schimmel & Co.[2]) are likewise of this opinion.

592. Oil of Eucalyptus dumosa.

Eucalyptus dumosa, H. Cunn.[5]), bull mallee, is indigenous to the dry interior of New South Wales, South Australia and Victoria. Baker and Smith[6]) describe its oil as an amber-colored product obtained with a yield of 1 p.c.: $d_{15°}$ 0.9016 to 0.9151; $[\alpha]_D$ + 2.44 to + 6.34°; $n_{D16°}$ 1.4760[1]); A.V. 0.63; E.V. 2.3; soluble in $1\frac{3}{4}$ vol. of 70 p.c. alcohol. The oil is rich in *cineol,* also contains *pinene* and *aromadendral* but no phellandrene. In connection with commercial oils Schimmel & Co. ascertained $d_{15°}$ 0.9211 to 0.9279; α_D + 9°26′ to — 5°13′; soluble in 1.5 to 2.4 vol. and more of 70 p.c. alcohol. Phellandrene reaction negative.

[1]) Smith, *loc. cit.* 45.
[2]) Report of Schimmel & Co. April 1905, 37.
[3]) Pharmaceutical Journ. 74 (1905), 143.
[4]) *Ibidem* 211.
[5]) According to Maiden (A critical revision of the genus Eucalyptus, vol. I. p. 97) *Eucalyptus dumosa*, A. Cunn. is synonymous with *E. incrassata*, Labill., var. *dumosa*, A. Cunn.
[6]) Research, p. 117. See also Bericht von Schimmel & Co. October 1889, 26.

593. Oil of Eucalyptus oleosa.

Eucalyptus oleosa, F. v. M. (*E. socialis*, F. v. M.; *E. turbinata*, Behr.) belongs to the shrubby eucalypts. It is indigenous to Queensland, Victoria, Western Australia and the western interior of New South Wales where it is known as red or water mallee. According to Baker and Smith[1]), the oil (yield 1.064 p.c.) is reddish orange-brown: d_{15° 0.925; $[\alpha]_D$ — 1.62°; n_{D16° 1.4746[2]); A. V. 3.4; E. V. 1.5; soluble in 1¹⁄₁ vol. of 70 p.c. alcohol. The principal constituent is *cineol*. *Pinene, aromadendral* and a *sesquiterpene* are the other known constituents. On standing, the oil deposits a solid substance. A sample said to have been derived from *Eucalyptus oleosa* was examined by Schimmel & Co. with the following results: d_{15° 0.9172; $\alpha_D + 0°3'$; soluble in 2.5 vol. and more of 70 p.c. alcohol.

594. Oil of Eucalyptus cneorifolia[3]).

The oil of this shrub-like species, a native of the Kangaroo Islands, first appeared in the market many years ago. An Adelaide firm which brought it into the market designated it as being derived from *Eucalyptus oleosa*. The explanation is that *E. cneorifolia*, D. C. was formerly regarded as a variety of *E. oleosa*[4]). d 0.899 to 0.923; α_D — 4° to - 14°; n_{D16° 1.4747[2])[5]). Baker and Smith[6]) record the following properties: d_{15° 0.9287; $[\alpha]_D$ — 5.82°; S. V. 16; soluble in 1¹⁄₄ vol. of 70 p.c. alcohol. The oil was rich in *cineol* and also contained *aromadendral*, and a *sesquiterpene*, but neither pinene nor phellandrene.

Two samples, one crude, the other rectified, examined by Schimmel & Co.[7]) had the following constants:—

	Color	d_{15}	α_D	sol. in 70 p.c. alcohol.
Crude oil . .	light brown	0.9192	— 7°25'	3.5 vol. and more.
Rect. oil . . .	yellow	0.9196	— 2°37'	2.5 vol. and more.

[1]) Research, p. 118. — Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 165.

[2]) Smith, *loc. cit.* 44.

[3]) Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 127.

[4]) Report of Schimmel & Co. April 1892, 59.

[5]) Wilkinson, Proceed. Royal Soc. of Victoria 1898, 198.

[6]) Research, p. 120, 219.

[7]) Report of Schimmel & Co. October 1913, 56.

Both oils were free from phellandrene. The eucalyptol content, determined by the resorcinol method, amounted to 41 p.c. for the crude oil and 64 p.c. for the rectified oil.

595. Oil of Eucalyptus stricta.

Eucalyptus stricta, Sieb. (*E. microphylla*, A. Cunn., *part.; E. Cunninghamii*, G. Don., part.) likewise belongs to the shrubby eucalypts and is indigenous to parts of New South Wales. Baker and Smith[1]) obtained 0.49 p.c. of oil: $d_{15°}$ 0.9246; $\alpha_D - 3.8°$; $n_{D16°}$ 1.4711[2]); A. V. 0.8; E. V. 1.7; soluble in $1^1/_4$ vol. of 70 p.c. alcohol. It contains very much *cineol*, also *pinene* and *eudesmol*.

Group IIIc.

Oils with more than 40 p.c. cineol containing phellandrene.

596. Oil of Eucalyptus melliodora.

Eucalyptus melliodora, A. Cunn., or yellow box is indigenous to the plateaus from Queensland to Victoria. According to Baker and Smith[3]) its oil, yield 0.866 p.c., consists exclusively of *cineol* and *pinene* with small amounts of *phellandrene*. $d_{15°}$ 0.9019 to 0.9046; $[\alpha]_D + 5.36$ to $+ 7.87°$; $n_{D16°}$ 1.4706[4]); S.V. 7.21 to 21.96; soluble in $1^1/_2$ vol. of 70 p.c. alcohol.

For an oil said to have been obtained from *Eucalyptus melliodora*, Schimmel & Co. record the following constants: $d_{15°}$ 0.9222; $\alpha_D + 6°50'$; $n_{D19°}$ 1.46110; soluble in 2 vol. of 70 p.c. alcohol.

597. Oil of Eucalyptus ovalifolia var. lanceolata.

Eucalyptus ovalifolia, R. T. Baker, var. *lanceolata*, Baker et Smith, which grows in the mountains of New South Wales,

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[1]) Research, p. 121.

[2]) Smith, *loc. cit.* 44.

[3]) Research, p. 122. See also Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 135. — Baker and Smith, Chemist and Druggist 57 (1900), 294. See also Parry, *ibidem* 58 (1901), 588; Report of Schimmel & Co. October 1901, 28.

[4]) Smith, *loc. cit.* 45.

yields 0.58 p.c. of an amber-colored oil[1]): $d_{15°}$ 0.9083; $[\alpha]_D$ — 4.7°; $n_{D16°}$ 1.4711[2]); A. V. 0.84; E. V. 3.03; soluble in 2 vol. of 70 p.c. alcohol. It consists principally of *cineol, pinene* and *phellandrene*.

598. Oil of Eucalyptus Risdoni.

Known as Risdon, drooping gum and blue peppermint, *Eucalyptus Risdoni*, Hook. f. grows in southern Tasmania. According to Baker and Smith[3]) the crude oil, yield 1.35 p.c., has the following properties: $d_{15°}$ 0.9045 to 0.9079; α_D — 0.33 to — 14.6°; $n_{D16°}$ 1.4733[4]); S. V. 21.1 to 23.8. It contains about 55 to 58 p.c. *cineol* (resorcinol method) and little *phellandrene*. Judging from the odor piperitone and amyl acetate are present.

In 1894 there was introduced into the London market an eucalyptus oil with a pleasant and mild odor which was termed Oil from *Eucalyptus Risdonia*; d 0,915 to 0,916; α_D — 4°49'. It contained *cineol* and *phellandrene*[5]).

599. Oil of Eucalyptus Gunnii.

The cider tree or cider gum, *Eucalyptus Gunnii*, Hook. f., grows in Tasmania. Baker and Smith[6]) describe the crude oil, yield 0.387 p.c., as a dark red liquid: $d_{15°}$ 0.9014; α_D + 1.5°; $n_{D18°}$ 1.4752; S.V. 6.7; soluble in 4 vol. of 80 p.c. alcohol. It contains 41 p.c. *cineol, d-pinene, l-phellandrene, esters* not further characterized, also *sesquiterpenes*.

600. Oil of Eucalyptus linearis.

White peppermint, *Eucalyptus linearis*, A. Cunn., also grows in Tasmania. Baker and Smith[7]) obtained 1.1 to 1.8 p.c. of oil,

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[1]) Baker and Smith, Research, p. 124.

[2]) Smith, *loc. cit.* 45.

[3]) Research, p. 208. — A research on the eucalypts of Tasmania, Hobart 1912, p. 35. See also Maiden, A critical revision of the genus Eucalyptus, vol. I, p. 172.

[4]) Smith, *loc. cit.* 44.

[5]) Report of Schimmel & Co. April 1894, 30.

[6]) A research on the eucalypts of Tasmania, Hobart 1912, p. 17; Report of Schimmel & Co. October 1913, 57.

[7]) A research on the eucalypts of Tasmania, Hobart 1912, p. 19; Report of Schimmel & Co. October 1913, 57.

the principal constituents of which are *cineol* (abt. 50 p.c.) and
l-*phellandrene*. In addition it contains *piperitone* and a *sesqui-
terpene*. This oil shows great similarity with that of *Eucalyptus
amygdalina* var. *Australiana*.

Group IV.

Oils with not more than 30 p.c. cineol and devoid of phellandrene, which consist principally of cineol, pinene and aromadendral.

601. Oil of Eucalyptus tereticornis.

Eucalyptus tereticornis, Smith, red gum or blue gum, is indi-
genous to a large part of eastern Australia. According to Baker
and Smith[1]) it yields 0.482 p.c. of oil. The orange-brown crude
oil has a decided odor of aromadendral. Phellandrene does not
occur in the oil but a small amount of *pinene* is found. The
cineol content was less than 5 p.c. In addition to *aromadendral* the
oil contains a fair amount of sesquiterpene. $d_{15°}$ 0.9218; $[\alpha]_D$ —10.2°;
$n_{D14°}$ 1.4934[2]); S.V. 26.7; soluble in an equal volume of 80 p.c.
alcohol.

In 1893 Schimmel & Co.[3]) described oil of *Eucalyptus
tereticornis* as being free of cineol, a statement contradicted
by the examination just recorded above.

Concerning oil of *Eucalyptus tereticornis* var. *linearis* see
p. 239.

602. Oil of Eucalyptus punctata var. didyma.

The var. *didyma*, Baker et Smith of *Eucalyptus punctata*,
D.C. is widely distributed over New South Wales. Baker and
Smith[4]) obtained a yield of 0.18 and 0.37 p.c. of oil which
contains 10 to 20 p.c. of *cineol*, also *aromadendral* and little
pinene. $d_{15°}$ 0.9033 to 0.907; $[\alpha]_D$ — 4.63 to — 6.53°; $n_{D16°}$ 1.4868[2]);
soluble in 7 vol. of 70 p.c. alcohol and in 2 vol. of 80 p.c. alcohol.

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1) Research, p. 126.
2) Smith, *loc. cit.* 46.
3) Report of Schimmel & Co. April 1898, 38.
4) Research, p. 127.

603. Oil of Eucalyptus gracilis.

As early as in the nineties Wilkinson[1]) made mention of the oil of *Eucalyptus gracilis*, F. v. M.[2]), a mallee shrub that is widely distributed over the Australian continent. From the leaves Baker and Smith[3]) obtained 0.901 p.c. of an amber-yellow oil consisting of a mixture of *cineol*, d-*pinene* and *aromadendral*. $d_{15°}$ 0.9098; $[\alpha]_D$ + 1.48°; $n_{D16°}$ 1.4771[1]); A. V. 3; E. V. 3.1; soluble in an equal vol. of 80 p.c. alcohol.

Wilkinson[1]) records d 0.909; $[\alpha]_D$ + 9.3'.

Whether preserved in the dark or exposed to daylight the oil deposits a solid substance, an observation that has also been made in connection with the oils of *Eucalyptus punctata, E. Cambagei, E. dumosa, E. Globulus, E. goniocalyx, E. hemilampra, E. intertexta, E. maculosa, E. oleosa, E. pendula, E. populifolia, E. quadrangulata* and *E. resinifera*. This white deposit is insoluble in the ordinary organic solvents with the exception of chloroform. Its formation is probably due to a constituent which these oils have in common. As to its composition nothing is known as yet.

604. Oil of Eucalyptus viridis.

Another mallee shrub, the *Eucalyptus viridis*, R. T. Baker[5]) is indigenous to a part of New South Wales, where it is known as green, red or brown mallee. Baker[6]) and Baker and Smith[7]) describe the oil of which they obtained a 1.06 p.c. yield, as an orange-brown liquid. It consists of *cineol* (less than 10 p.c.), l-*pinene* and *aromadendral*. Phellandrene was not present,

[1]) Proceed. Royal Soc. of Victoria 1893, 197.

[2]) According to Maiden (A critical revision of the genus Eucalyptus, vol. I. p. 79) *E. gracilis* is synonymous with *E. calycogona*, Turcz. var. *celastroides*, Maiden.

[3]) Research, p. 129.

[4]) Smith, *loc. cit.* 45.

[5]) According to Maiden (A critical revision of the genus Eucalyptus, vol. II. p. 45) *E. viridis* is synonymous with *E. acacioides*, A. Cunn. and with *E. odorata*, Behr var. *linearis*, Maiden.

[6]) Proceed. Linnean Soc. of N. S. W. 1900, 316; Report of Schimmel & Co. October 1901, 28.

[7]) Research, p. 131.

$d_{15°}$ 0.9006; $[\alpha]_D$ --8.9°; $n_{D16°}$ 1.4828[1]); A. V. 2.76; E. V. 2.97; soluble in 2 vol. of 80 p.c. alcohol.

605. Oil of Eucalyptus Woollsiana.

Eucalyptus Woollsiana, R. T. Baker, a mallee box, grows in parts of New South Wales. Baker and Smith[2]) distilled the oil with a yield of 0.44 to 0.52 p.c. It contains very little *cineol* and no phellandrene, but *pinene* and *aromadendral*. $d_{15°}$ 0.8890 to 0.9051; $[\alpha]_D$ — 10.65 to — 17.66°; $n_{D16°}$ 1.4895[1]); A. V. 2.2; E. V. 6.9; soluble in an equal volume of 80 p.c. alcohol.

606. Oil of Eucalyptus albens.

White box, *Eucalyptus albens*, Miq.[3]), is indigenous to a part of New South Wales. From the leaves Baker and Smith[4]) obtained 0.1 p.c. of oil which contained a fair amount of *cineol*, also *aromadendral*, but no phellandrene. $d_{15°}$ 0.9044; $[\alpha]_D$ --7.2°; $n_{D16°}$ 1.4836[1]); A. V. 3.3; E. V. 5.2; soluble in an equal volume of 80 p.c. alcohol.

607. Oil of Eucalyptus hemiphloia.

Eucalyptus hemiphloia, F. v. M.[5]) is a common box in eastern South Australia, Victoria, New South Wales and southern Queensland. According to Schimmel & Co.[6]) this reddish-brown oil contains much *cineol* and a large amount of *cuminic aldehyde*. Baker and Smith[7]) enumerate *cineol, pinene* and *aromadendral* as constituents and record the following properties: $d_{15°}$ 0.9117; $[\alpha]_D$ — 7.46; $n_{D16°}$ 1.4910[1]); A. V. 1.81; E. V. 4; soluble in 2 vol. of 70 p.c. alcohol. The yield amounted to 0.57 p.c.

[1]) Smith, *loc. cit.* 46.

[2]) Proceed. Linnean Soc. of N. S. W. 1900, 684; Report of Schimmel & Co. April 1902, 40. — Research, p. 132.

[3]) Maiden (A critical revision of the genus Eucalyptus, vol. II. p. 20) regards *E. albens* as a variety of *E. hemiphloia* and names it *E. hemiphloia*, F. v. M. var. *albens*, F. v. M.

[4]) Research, p. 134.

[5]) Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 14.

[6]) Report of Schimmel & Co. April 1898, 38.

[7]) Research, p. 136.
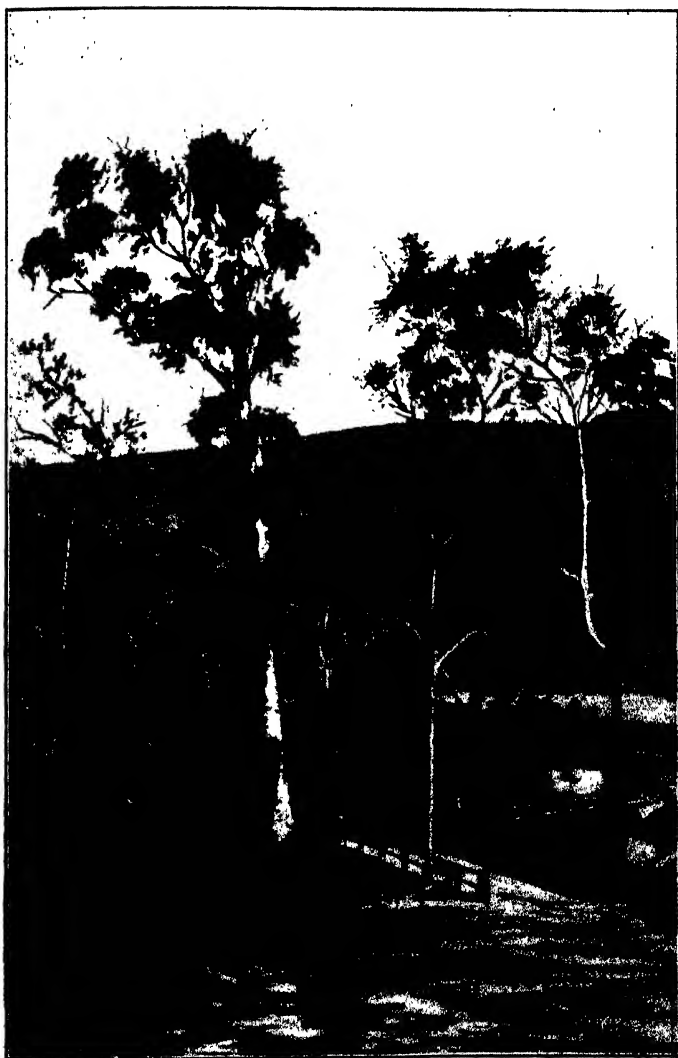
Fig. 21. A group of eucalyptus trees at the foot of the Blue Hills (Australia).

From this oil, also from that of *Eucalyptus salubris,* Baker and Smith[1]) obtained an apparently new aldehyde. W. Anderson having coined the word *Aromadendron* for the genus *Eucalyptus,* they modified it to *aromadendral.* Their first formula $C_{10}H_{14}O$ was later replaced by the formula $C_9H_{12}O$. After removing those portions of the oil that boiled below 195˚ they isolated the aldehyde by shaking the higher portion with bisulphite solution. It constitutes a yellowish readily mobile liquid, the odor of which is not unpleasant but somewhat more aromatic than cuminic aldehyde, boiling between 210 and 215˚; $d_{15°}$ 0.9478; $[\alpha]_{D22°}$ —49.19° (from oil of *E. hemiphloia*); b.p. 218 to 219˚ (with partial decomposition); $d_{16°}$ 0.9576; $d_{22°}$ 0.9533; $[\alpha]_{D22°}$ —90.43 ; $n_{D16°}$ 1.5141; mol. refr. found 42.76, computed for $C_9H_{12}O/_3$ 42.53 (from oil of *E. salubris*).

The oxime of this aldehyde melted at 86˚; the phenylhydrazone, when prepared in acetic acid solution, melted at 104 to 105°; the phenylhydrazone prepared in alcoholic or petroleum ether solution melted somewhat higher but was unstable; the naphthocinchoninic acid melted at 245 to 246˚.

Aromadendral readily adds bromine with the formation of a liquid dibromide ($d_{22°}$ 1.4302). Upon heating it splits off hydrogen bromide, probably with the formation of a monobromide.

Oxidized with potassium bichromate and sulphuric acid aromadendral yields an unsaturated, monobasic acid, aromadendric acid, $C_9H_{12}O_2$. Dried at 105 to 110°, the acid melted at 137 to 138°, a slight amount of sublimation being observable. The air-dried crystals melted at a lower temperature but revealed no constant melting point. The acid is almost insoluble in cold water, slightly soluble in hot water, readily soluble in alcohol and ether.

Treated with alkaline permanganate the aldehyde undergoes a fairly energetic reaction with the evolution of considerable heat. According to Smith, one of the oxidation products is presumably cineol (?); another is an acid that melts at 259 to 260˚ and which, upon heating, is converted into its anhydride that melts at 152°, hence cannot be identical with cineolic acid.

¹) Journ. and Proceed. Royal Soc. of N. S. W. 34 (1900), 1; Report of Schimmel & Co. April 1901, 34; October 1901, 24.—Research, p. 218.—Pharmaceutical Journ. 75 (1905), 382.

According to C. Hall[1]) aromadendral has decided antiseptic properties.

The observation that the aldehydes isolated from various eucalyptus oils differ greatly as to optical rotation led Baker and Smith to infer that aromadendral occurs in both optical modifications. The same conclusion is reached from the similarity of the oximes, hydrazones and naphthocinchoninic acids obtained from aromadendrals of varying angles of rotation. On the other hand these investigators regard it as possible that cuminic aldehyde may likewise be present as is the case in the oil of *E. hemiphloia* where its presence has been demonstrated beyond doubt by Schimmel & Co.[2]).

From an Australian eucalyptus oil, probably *E. odorata,* Schimmel & Co. obtained, by shaking with sodium acid sulphite solution, 0.25 p.c. of an aldehyde, which upon careful investigation, proved to be cuminic aldehyde. Inasmuch as the bisulphite addition compound, because of its slimy character, could be purified only with great difficulty with alcohol and ether, it was dissolved in water and the aqueous solution purified by repeated extraction with ether. The aldehyde, liberated from this solution and isolated by steam distillation, boiled between 50 (17 mm.) and 85 (5 mm.), an appreciable portion, however, between 82.5 and 84 (5 mm.). This portion was almost colorless and had the odor of cuminic aldehyde. Fraction 82.5 to 84 (5 mm.) had the following physical constants: b.p. 228 to 238; $d_{15°}$ 0.9828; $\alpha_D + 0°$. Very striking was the property to oxidize in a short time when exposed to the air. In acetic acid solution the aldehyde formed a semicarbazone melting between 202 and 207°. The phenylhydrazone, recrystallized from ligroin, melted at 126 to 127°, the oxime at 58. Oxidized with permanganate cuminic acid, m.p. 116 to 117′, was formed. A mixture of cuminic acid with this acid had the same melting point. Hence there can scarcely be a doubt as to the identity of this aldehyde with cuminic aldehyde.

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[1]) On eucalyptus oils, especially in relation to their bactericidal power. Parramatta 1904, p. 16; Report of Schimmel & Co. October 1904, 37.

[2]) Report of Schimmel & Co. October 1905, 36. — See also oil of *Eucalyptus odorata,* p. 290; Bericht von Schimmel & Co. April 1889, 19.

608. Oil of Eucalyptus Rudderi.

To this group there also belongs *Eucalyptus Rudderi*, Maiden, a red gum[1]) of New South Wales. From the fresh leaves and twigs Baker and Smith[2]) obtained 0.3 p.c. of crude oil with the characteristic odor of the box oils and a by-odor of aromadendral. Its constants are: $d_{16°}$ 0.942; α_D — 8.5′; $n_{D20°}$ 1.4898; soluble in 1 vol. of 80 p.c. (percentage by weight) alcohol. The oil contains only small amounts of *cineol* (about 5 p.c.) and scarcely any pinene. The lævorotation seems to be due to *aromadendral*. Phellandrene is wanting.

Group V.

Oils which consist of pinene, cineol and phellandrene and which contain not more than 30 p.c. of cineol.

609. Oil of Eucalyptus viminalis.

Eucalyptus viminalis, manna or white gum, is possibly the tallest of the eucalypts, trees with a height of 300 ft. having been measured. This species occurs in New South Wales, South Australia, Victoria and Tasmania. From the leaves Baker and Smith[3]) obtained from 0.35 to 0.14 p.c. of a very dark oil which consisted of *cineol* (50 p.c., according to resorcinol method), *phellandrene, aromadendrene* and d-*pinene*: $d_{15°}$ 0.9044 to 0.9162; α_D + 3.96 to + 4.2°; $n_{D16°}$ 1.4855[4]), $n_{D19°}$ 1.4711; S.V. 9.5; soluble in an equal volume of 80 p.c. alcohol.

An oil described by Wittstein ·and Müller[5]) as having been obtained from *E. viminalis* (author's name not given) differs so much from the one described above that it cannot be assumed as having been obtained from the same species. The odor of the oil was unpleasant; d 0.921; it boiled between 159 and 182°.

[1]) Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 118.

[2]) Proceed. Linnean Soc. of N. S. W. 1906, 714; Report of Schimmel & Co. November 1906, 67.

[3]) Research, p. 137, 246. — A research on the eucalypts of Tasmania, Hobart 1912, p. 43.

[4]) Smith, *loc. cit.* 47.

[5]) Maiden, The useful native plants of Australia, p. 275. London and Sydney 1889.

610. Oil of Eucalyptus rostrata.

Eucalyptus rostrata, Schlecht, Murray red gum, which in Australia occurs along the shores of the Murray, Lachlan and Murrumbidgee rivers, has been cultivated on a large scale in southern France, German Southwest Africa[1]), also in Algeria, where it is said to resist the heat better than *Eucalyptus Globulus.* According to Maiden[2]) the fresh leaves yield but 0.1 p.c.; according to Baker and Smith[3]) from 0.137 to 0.4 p.c. of oil: d 0.912 to 0.925; $\alpha_D - 1°8'$ to $-13°$[4]); $d_{15°}$ 0.8953 to 0.9065; $[\alpha]_D - 13.05$ to $-16.98°$; $n_{D16°}$ 1.4896[5]); soluble in 1 to 2 vol. of 80 p.c. alcohol. In connection with several commercial oils Schimmel & Co. found the following constants: $d_{15°}$ 0.9215 to 0.9288; $\alpha_D - 0°6'$ to $-2°58'$; soluble in 2 to 4.5 vol. of 70 p.c. alcohol. All of the oils examined by Schimmel & Co. were free from phellandrene. An oil obtained by this firm from Algeria[6]) had a decided odor of valeric aldehyde and contained a large amount of *cineol.* Baker and Smith[3]) mention *cineol* and *aromadendral* as constituents. The presence of phellandrene cannot always be detected for it seems to be dependent on the season.

611. Oil of Eucalyptus ovalifolia.

Eucalyptus ovalifolia, R. T. Baker is indigenous to a part of New South Wales. The leaves yield 0.27 p.c. of oil which contains much *phellandrene,* relatively much *sesquiterpene* and but little *pinene* and *cineol.* In the fresh oil Baker and Smith[7]) could detect but little cineol, but after it had stood for 18 months 18 p.c. of this substance was found.

In connection with the crude oil the following constants were found: $d_{15°}$ 0.9058; $[\alpha]_D - 9.93°$; $n_{D16°}$ 1.4921[8]); A.V. 1.4; E.V. 4.8; soluble in 1 vol. of 80 p.c. alcohol.

[1]) Report of Schimmel & Co. April 1908, 54.

[2]) The useful native plants of Australia. London and Sydney 1889, p. 273.

[3]) Research, p. 139.

[4]) Wilkinson, Proceed. Royal Soc. of Victoria 1898, 197, 198.

[5]) Smith, *loc. cit.* 46.

[6]) Report of Schimmel & Co. October 1891, 51.

[7]) Research, p. 140. — Baker, Proceed. Linnean Soc. of N. S. W. 1900, 680; Report of Schimmel & Co. April 1902, 39.

[8]) Smith, *loc. cit.* 47.

612. Oil of Eucalyptus Dawsoni.

The oil of *Eucalyptus Dawsoni*, R. T. Baker, slaty gum, a species indigenous to New South Wales, has been described by Baker and Smith[1] as an orange-brown, viscid liquid, the principal constituent of which is *aromadendrene*. It also contains *phellandrene* and a little *cineol*. The yield was 0.172 p.c.; d_{15° 0.9418; S. V. 13.3; n_{D16° 1.5144[2]); soluble in 2 vol. of 80 p.c. alcohol.

613. Oil of Eucalyptus angophoroides.

Apple-top box is the name by which *Eucalyptus angophoroides*, R. T. Baker (*E. Bridgesiana*, part.) is known in New South Wales in parts of which it is indigenous. According to Baker and Smith[3] the yield of the red oil is 0.185 p.c. It contains much *phellandrene* and *sesquiterpene*, also *cineol* and *pinene*. d_{15} 0.9049; $[\alpha]_D$ 12.7°; n_{D16} 1.4881[2]); A.V. 3.7; E.V. 3.6; soluble in an equal volume of 80 p.c. alcohol.

614. Oil of Eucalyptus fastigata.

In Victoria and New South Wales there occurs the cut tail, *Eucalyptus fastigata*, Deane et Maiden, the oil of which, yield 0.11 p.c., was distilled by Baker and Smith[1] and for which they record the following constants: d_{15} 0.8925 to 0.9001; n_{D16° 1.4873[2]); A.V. 4.9; E.V. 7.5 to 10; soluble in 5 vol. of 80 p.c. alcohol. In another instance the oil did not yield a clear solution with 10 vol. of 80 p.c. alcohol. d-*Pinene*, *phellandrene*, *eudesmol* and *cineol* are the constituents identified.

615. Oil of Eucalyptus macrorrhyncha.

The oil of the leaves of *Eucalyptus macrorrhyncha*, F. v. M., known as red stringy bark in New South Wales, has been exa-

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[1]) Research, p. 142, 246. — Baker, Proceed. Linnean Soc. of N. S. W. 1899, 295; Report of Schimmel & Co. April 1900, 27.

[2]) Smith, *loc. cit.* 47.

[3]) Research, p. 143. — Baker, Proceed. Linnean Soc. of N. S. W. 1900, 676; Report of Schimmel & Co. April 1902, 39.

[4]) Research, p. 145, 212.

mined by Baker and Smith[1]). They obtained a yield of 0.29 to 0.3 p.c.; d_{15} 0.929; $n_{D16°}$ 1.4802[2]). It contains *cineol*, also *phellandrene, pinene, eudesmol* and a *sesquiterpene*. Baker and Smith[3]) used this oil as the source of larger quantities of *eudesmol*. Having removed by distillation the fractions below 190°, eudesmol separated from the residue as a butyraceous, crystalline mass. After recrystallization from diluted alcohol it was obtained in silky needles melting at 79 to 80°. Eudesmol is insoluble in water and aqueous alkali, readily soluble in the ordinary organic solvents. It sublimes readily and is optically inactive. Elementary analysis and molecular weight determinations, according to the freezing point method, revealed the formula $C_{10}H_{16}O$, hence an isomer of ordinary camphor.

Acted upon by strong nitric acid in the cold, eudesmol yields an uncrystallizable dinitro product, $C_{10}H_{14}(NO_2)_2O$. Brominated in glacial acetic acid solution in the cold, it yielded an amorphous dibromide $C_{10}H_{16}Br_2O$, m. p. 55 to 56°, which could no more be made to crystallize than the dinitro compound.

Oxidized with diluted nitric acid, eudesmol yielded an acid melting between 165 and 168° which Baker and Smith regard as *i*-camphoronic acid.

Whereas Baker and Smith regard eudesmol as an oxide $C_{10}H_{16}O$, F. W. Semmler and E. Tobias[4]) have ascertained that it is in reality a bicyclic, unsaturated sesquiterpene alcohol. For its constants the following values have been recorded: m.p. 78°; b.p. 156° (10 mm.); $d_{20°}$ 0.9884; $[\alpha]_{D20°}$ +31°21′ (in 12 p.c. chloroform solution); $n_{D20′}$ 1.516; mol. refr. computed for $C_{15}H_{26}O$ 68.069, found 67.85. This molecular refraction reveals the presence of a double bond and two cycles in eudesmol. Upon acetylation it yields an acetate b.p. 165 to 170° (11 mm.) the physical constants of which likewise reveal its bicyclic nature and the presence

[1]) Research, p. 146. — Journ. and Proceed. Royal Soc. of N. S. W. **32** (1898), 105; Report of Schimmel & Co. April 1899, 23. See also Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 225.

[2]) Smith, *loc. cit.* 47.

[3]) Research, p. 213. — Journ. and Proceed. Linnean Soc. of N. S. W. **33** (1899), 86; Report of Schimmel & Co. April 1900, 27.

[4]) Berl. Berichte **46** (1913), 2026. See also Semmler and Mayer, *ibidem* **45** (1912), 1390.

of a double bond. Reduction in ethereal solution with hydrogen and platinum sponge yielded dihydroeudesmol, an alcohol that melted at 82°; b.p. 155 to 160° (12.5 mm.); b.p. of the acetate 158 to 164° (10 mm.). Boiled with absolute formic acid, dihydroeudesmol yields dihydroeudesmene boiling between 126 and 130° (10 mm.). When eudesmol is boiled with 90 p.c. formic acid, it is dehydrated to eudesmene, b.p. 129 to 132° (10 mm.); $d_{20°}$ 0.9204; $[\alpha]_{D20°} + 49°$; $n_{D20°}$ 1.50738. The molecular refraction of eudesmene reveals the presence of 2 cycles and 2 double bonds. Hence it belongs to that group of sesquiterpenes which is derivable from reduced naphthalene, to which group cadinene, selinene, *iso*zingiberene, &c. belong. When eudesmol is shaken with a solution of hydrogen chloride in glacial acetic acid, eudesmene dihydrochloride, m.p. 79 to 80°, results, which is identical with the hydrogen chloride addition product of eudesmene. Eudesmene dihydrobromide melts at 104 to 105°. Oxidation of eudesmol with ozone and with potassium permanganate gave no satisfactory results.

Semmler and F. Risse[1]) report on another method for the preparation of eudesmene. The glacial acetic acid solution of eudesmol, 1 to 4, is saturated with hydrogen chloride. Upon evaporation of the glacial acetic acid in vacuum eudesmene hydrochloride remains. Boiled with alcoholic potassa the hydrochloride yields eudesmene with the following properties: b.p. 122 to 124° (7 mm.); $d_{20°}$ 0.9196; $[\alpha]_D + 54° 6'$; n_D 1.50874. Reduced with platinum hydrogen in glacial acetic acid solution eudesmene yields tetrahydroeudesmene, b.p. 122 to 122.5° (75 mm.); $d_{20°}$ 0.8893; $[\alpha]_D + 10° 12'$; n_D 1.48278.

These same authors show that the reduction of eudesmol in glacial acetic acid solution by means of platinum-hydrogen takes a different course than the one in ethereal solution previously described. Inasmuch as previous investigations have revealed the fact that the activity of the platinum is greatly impaired by impurities of the substance to be reduced, such as traces of resinous products, the eudesmol was purified of the last traces of resins by shaking its ethereal solution with alkali and recrystallization from diluted alcohol to which a few drops of glacial acetic acid had been added. Eudesmol thus purified melted at 84°.

[1]) Berl. Berichte 46 (1913), 2303.

Tetrahydroeudesmene (b.p. 116 to 117° (5.5 mm.); d_{20} 0.8896; $[\alpha]_D + 11°48'$; n_D 1.48425) again resulted as reduction product. Hence the reduction of eudesmol in glacial acetic acid resulted not only in the addition of hydrogen to the double bond but also in the replacement of the hydroxyl group by hydrogen, whereas the reduction previously described had resulted in a dihydroeudesmol.

In its physical constants eudesmene shows some correspondence with those of selinene. For this reason eudesmene was ozonized in acetic acid solution, however, without positive results for the investigation did not succeed in isolating any characteristic "Abbau" products.

The bactericidal action of eudesmol has been investigated by C. Hall[1]). It seems that, added to cineol or piperitone, it increases the action of these substances.

The cineol content of the eucalyptus oils varies with the maturity of the leaves when distilled. Smith also holds that the cineol content of eudesmol-containing oils increases with age provided atmospheric oxygen has access. He therefore assumes that eudesmol is an intermediate product in the formation of cineol.

616. Oil of Eucalyptus capitellata.

As ascertained by Baker and Smith[2]), brown stringy bark, *Eucalyptus capitellata*, Sm., a species that is distributed over New South Wales, South Australia and Victoria, yields only 0.1 p.c. of oil. It consists of *cineol, phellandrene, pinene* and a *sesquiterpene*: $d_{15°}$0.9175; $[\alpha]_D + 4.8°$; $n_{D16°}$1.4828·)); S. V. 4.27; soluble in 10 vol. of 70 p.c. alcohol, soluble in an equal volume of 80 p.c. alcohol.

617. Oil of Eucalyptus nigra.

Black stringybark, *Eucalyptus nigra*, R. T. Baker, inhabits a large part of New South Wales. The oil yield is very small,

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[1]) On eucalyptus oils, especially in relation to their bactericidal power. Parramatta 1904; Report of Schimmel & Co. October 1904, 37.

[2]) Journ. and Proceed. Linnean Soc. of N. S. W. 32 (1898), 106; Report of Schimmel & Co. April 1899, 24. — Research, p. 149. See also Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 211.

[3]) Smith, *loc. cit.* 47.

Baker and Smith[1]) obtained but 0.041 p.c. from the leaves. It was amber-yellow in color, contained not more than 5 p.c. of *cineol* and a large amount of *phellandrene:* $d_{15°}0.8744$; $[\alpha]_D - 38.88°$; $n_{D16°}1.4871^2$); A. V. 7.2; with 10 vol. of 80 p.c. alcohol it does not form a clear solution.

618. Oil of Eucalyptus pilularis.

Eucalyptus pilularis, Smith, or black butt, is one of the tall eucalypts. It is a native of the coastland as well as the plateaus of New South Wales and also occurs in Victoria and Queensland. Baker and Smith[3]) obtained 0.07 to 0.18 p.c. of a light amber-colored oil which contained much l-*phellandrene,* a *sesquiterpene,* traces of *cineol* and *pinene,* and probably a dextrorotatory alcohol. $d_{15°}0.885$ to 0.903; $[\alpha]_D - 4.8$ to $+12.3°$; $n_{D16°}1.4961^2$); for the most part soluble in 8 vol. of 80 p.c. alcohol, but occasionally does not form a clear solution with even 10 volumes.

619. Oil of Eucalyptus Planchoniana.

Eucalyptus Planchoniana, F. v. M., one of the stringybarks, occurs in parts of New South Wales and Queensland. According to Staiger[4]) it yields 0.06 p.c. of oil with a density of 0.915. Baker and Smith[5]) obtained but 0.014 p.c. of oil which contained relatively much *phellandrene* and *sesquiterpene.* Cineol was not found. $d_{15°}0.9039$; $n_{D16°}1.4878^2$); A. V. 4.2; E. V. 2.9; insoluble in 10 vol. of 80 p.c. alcohol.

620. Oil of Eucalyptus acmenoides.

White mahogany or *Eucalyptus acmenoides,* Schau. (*E. triantha,* Link[6])) grows in Queensland and in the coastal regions

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[1]) Research, p. 150.

[2]) Smith, *loc. cit.* 47.

[3]) Research, p. 151. See also Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 26.

[4]) Maiden, The useful native plants of Australia, p. 273. London and Sydney 1889.

[5]) Research, p. 153. See also Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 291.

[6]) Maiden, *loc. cit.* 263.

of New South Wales. Baker and Smith[1]) distilled the oil with a yield of 0.09 p.c. It contained much *aromadendrene* (see p. 274), *phellandrene*, little *cineol* and possibly pinene. $d_{15°}0.9252$; $n_{D18°}1.5065$[2]); A. V. 5.7; E. V. 2.9; soluble in an equal volume of 80 p.c. alcohol.

621. Oil of Eucalyptus fraxinoides.

Eucalyptus fraxinoides, Deane et Maiden, known in New South Wales as white ash, yields, according to Baker and Smith[3]) 0.985 p.c. of oil which, even in the crude condition, is but slightly colored. It consists principally of *phellandrene*, but in addition it contains *pinene*, *eudesmol*, about 5 p.c. *cineol* and possibly some citral. $d_{15°}0.8687$; $[\alpha]_D - 31.66°$; $n_{D16°}1.4908$[4]); A. V. 1; E. V. 2.86; does not yield a clear solution with 10 vol. of 80 p.c. alcohol.

622. Oil of Eucalyptus Fletcheri.

Eucalyptus Fletcheri, R. T. Baker, *lignum vitæ*, or box, is distributed over New South Wales. It yields 0.294 p.c. of oil in which, according to Baker and Smith[5]) l-*phellandrene* and a *sesquiterpene* predominate. Other constituents are *cineol* (less than 5 p.c.), *pinene* and *aromadendral*. $d_{15°}0.8805$ to 0.895; $[\alpha]_D - 14.2°$; $n_{D16°}1.4881$[2]); A. V. 1.1 to 2.3; E. V. 2.2 to 3.19; soluble in 2 vol. of 80 p.c. alcohol, but occasionally insoluble even in 10 vol. of 80 p.c. alcohol.

623. Oil of Eucalyptus microtheca.

Eucalyptus microtheca, F. v. M.[6]) (*E. brachypoda*, Turcz. part.), known as *coolybah* or *tangoon*, inhabits a large part of the Australian continent. According to Baker and Smith[7]) the crude oil, obtained with a yield of 0.488 p.c., is a reddish

[1]) Research, p. 154, 246.
[2]) Smith, *loc. cit.* 47.
[3]) Research, p. 155.
[4]) Smith, *loc. cit.* 46.
[5]) Research, p. 157. — Baker, Proceed. Linnean Soc. of N. S. W. 1900, 682; Report of Schimmel & Co. April 1902, 40.
[6]) Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 51.
[7]) Research, p. 158.

liquid. It contains much *phellandrene*, a *sesquiterpene*, little *pinene* and a trace of *cineol* (characterized by its iodol derivative). $d_{15°}$ 0.8855; $[\alpha]_D$ —30.72°; $n_{D16°}$ 1.4895[1]); A.V. 1.34; E.V. 3; does not form a clear solution with 10 vol. of 80 p.c. alcohol.

624. Oil of Eucalyptus hæmastoma.

Eucalyptus hæmastoma, Sm. (*E. signata*, F. v. M.[2])), white or scribbly gum, occurs over large areas in New South Wales, also in Tasmania, Victoria and Queensland. Baker and Smith[3]) obtained 0.28 p.c. of oil, which is said to contain much *phellandrene*, *cineol* and very much *aromadendrene*. $d_{15°}$ 0.9195; A.V. 1.9; E.V. 3.2; $n_{D16°}$ 1.5013[1]); with 10 vol. of 80 p.c. alcohol it does not yield a clear solution. In 1888 Schimmel & Co.[4]) reported on an oil of *E. hæmastoma*, 1.8 to 1.9 p.c. of which had been obtained from fresh leaves. It had a peppermint-like odor which at the same time reminded of geranium and cumin. d 0.880 to 0.890; boiling temperature 170 to 250°. It contained cineol, terpenes and possibly cuminic aldehyde and menthone. These statements do not at all agree with those of Baker and Smith. Presumably the oil examined by the firm mentioned was obtained from another species, possibly from *Eucalyptus Rossii*[5]).

From the oil of *E. hæmastoma*, Baker and Smith[6]) obtained larger amounts of *aromadendrene*[7]). Purified as carefully as possible by repeated distillation over sodium, the product boiled between 260° and 265°; $d_{19°}$ 0.9249. Its glacial acetic acid solution yields a rose-red color with phosphoric acid. This explains the red color frequently produced in the cineol assay according to the phosphoric acid method. Up to the present time aromadendrene has been characterized by color reactions only. Solid

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[1]) Smith, *loc. cit.* 47.

[2]) Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 317.

[3]) Research, p. 160.

[4]) Bericht von Schimmel & Co. April 1888, 20.

[5]) Research, p. 12, 229.

[6]) Journ. and Proceed. Royal Soc. of N.S.W. 35 (1901), 124; Report of Schimmel & Co. April 1902, 41. — Research, p. 246.

[7]) The presence of aromadendrene in the turpentine oil of *Pinus Lambertiana*, Dougl. does not seem improbable. (A. W. Schorger, U. S. Dep. of Agricult. Forest Serv. Bull. 119. Washington 1913; Report of Schimmel & Co. April 1913, 102.)

derivatives are unknown. According to Baker and Smith the color reaction produced by bromine may serve for the detection of aromadendrene. For this purpose a drop or two of aromadendrene are dissolved in 2 to 3 ccm. of glacial acetic acid contained in a test tube and bromine vapors are allowed to descend down the tube. Upon shaking, the solution assumes a carmine-red color. The color soon changes to violet and finally to indigo-blue.

According to Semmler[1]) aromadendrene is possibly a mixture of bi- and tricyclic sesquiterpenes. The color reactions it has in common with several bicyclic sesquiterpenes, e. g. guajene.

C. Hall[2]) has examined aromadendrene pharmacologically and has found that it has fairly decided germicidal powers.

625. Oil of Eucalyptus sideroxylon var. pallens.

Eucalyptus sideroxylon, A. Cunn. var. *pallens*, Benth., or ironbark, grows only in the vicinity of Rylstone (N. S. W.). It yields 0.4 p. c. of a dark amber-colored oil which consists of *phellandrene, pinene, cineol,* and a *sesquiterpene.* $d_{15°}$ 0.9158; $[\alpha]_D + 13.9°$; $n_{D16°}$ 1.4884[3]); A.V. 1.8; E.V. 4.6; soluble in an equal volume of 80 p. c. alcohol[4]).

626. Oil of Eucalyptus crebra.

As early as 1893 Schimmel & Co.[5]) reported on the oil of *Eucalyptus crebra*, F. v. M., the narrow-leaved ironbark of New South Wales, Queensland and northern Australia. Later on the oil was investigated by Baker and Smith[6]), who obtained a yield of 0.16 p. c. It contained much *phellandrene* and *cineol,* also *aromadendrene.* $d_{15°}$ 0.8986; $[\alpha]_D - 12.1°$; $n_{D16°}$ 1.4844[3]); A. V. 1.65; E.V. 4.6; it does not yield a clear solution with 10 vol. of 80 p. c. alcohol.

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[1]) *Die ätherischen Öle,* vol. II. p. 530.

[2]) On eucalyptus oils, especially in relation to their bactericidal power. Parramatta 1904; Report of Schimmel & Co. October 1904, 37.

[3]) Smith, *loc. cit.* 47.

[4]) Research, p. 161.

[5]) Report of Schimmel & Co. April 1893, 38.

[6]) Research, p. 162, 246. — Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 63.

For an oil, said to have been derived from *Eucalyptus crebra* of the Tengger mountains of Java, Schimmel & Co.[1]) obtained the following constants: d_{15° 0.9036; α_D — $20^\circ 56'$; with 5 to 6 vol. and more of 80 p. c. alcohol it yielded a turbid solution. In addition to little *cineol*, the oil contained *phellandrene* and *cuminic aldehyde*.

627. Oil of Eucalyptus siderophloia.

Eucalyptus siderophloia, Benth.[2]) inhabits the coast regions from Port Jackson to Queensland and is known as broad-leaved or red ironbark. According to Baker and Smith[3]) it yields 0.056 p. c. of oil, which in the crude condition is lemon-yellow. It contains much *phellandrene*, also *pinene* and *cineol*. d_{15° 0.9067; $[\alpha]_D + 15.98^\circ$; n_{D16° 1.5000[4]); S.V. 4; S.V. after acetylation 41.9; it does not yield a clear solution with 10 vol. of 80 p. c. alcohol.

628. Oil of Eucalyptus melanophloia.

Eucalyptus melanophloia, F. v. M., which is distributed over parts of New South Wales and also occurs in Queensland, is commonly known as silver-leaved ironbark. In the oil, yield 0.105 p. c., Baker and Smith[5]) found very much *phellandrene, sesquiterpene, cineol* (iodol compound) and p-*cymene* (characterized by oxidation to terephthalic acid and p-toluic acid). d_{15° 0.8959; $[\alpha]_D$ — 26.23°; n_{D16° 1.4950[4]); A.V. 0.9; E.V. 10.1; S.V. after acetylation 27.87; with 10 vol. of 80 p. c. alcohol it does not yield a clear solution.

629. Oil of Eucalyptus phlebophylla.

The oil of *Eucalyptus phlebophylla*, F. v. M., cabbage or weeping gum, was distilled by Baker and Smith[6]) with a yield of about 1 p. c. d_{15° 0.8766 to 0.8925; α_D — 22.4 to — 32.5°;

[1]) Report of Schimmel & Co. April 1909, 53.

[2]) Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 324.

[3]) Research, p. 163.

[4]) Smith, *loc. cit.* 47.

[5]) Research, p. 164. See also Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 71.

[6]) A research on the eucalypts of Tasmania, Hobart 1912, p. 27; Report of Schimmel & Co. October 1913, 57.

$n_{D15°}$ 1.4702; $n_{D18°}$ 1.4761; S. V. 3.2. The oil contains 50 to 60 p.c. l-*α-pinene* (nitrosochloride), 9 to 11 p.c. *cineol*, also *phellandrene* and *eudesmol* and probably a *sesquiterpene*.

630. Oil of Eucalyptus regnans.

Swamp gum, *Eucalyptus regnans*, F. v. M. (*E. gigantea*, Hook. *part.*), occurs in Tasmania. According to Baker and Smith[1]) it yields 0.78 to 0.82 p. c. of oil; $d_{15°}$ 0.8802 and 0.8878; $α_D$ -- 28.4 and —31.1°; $n_{D20°}$ 1.4882 and 1.4901; S. V. 13.2 and 15.4; soluble in 5 vol. of 70 p. c. alcohol. *Phellandrene* is the principal con-
stituent. *Eudesmol, geranyl acetate, piperitone*, a *sesquiterpene* and possibly traces of *cineol* are likewise present.

Group VIa.

Oils which consist principally of phellandrene, cineol (up to 30 p.c.) and piperitone.

631. Oil of Eucalyptus piperita.

The oil of the leaves of *Eucalyptus piperita*, Sm. (*Metrosideros aromatica*, Salisb.), a species indigenous to New South Wales, Queensland and Victoria, was known as early as 1788. It is mentioned on p. 266 of White's Journal of a voyage of New South Wales, where the following statement occurs: "The name peppermint tree[2]) was given to this plant by White because of the great similarity of the oil of the leaves to that of the peppermint grown in England".

More recently the oil has been distilled by Baker and Smith[3]), the leaves and twigs yielding 0.78 p. c. It is of a yellow color and has a pronounced peppermint odor, which, however, becomes faint after the oil has stood several weeks. It is in this oil that Baker and Smith first found *eudesmol*. Other constituents are

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[1]) A research on the eucalypts of Tasmania, Hobart 1912, p. 31; Report of Schimmel & Co. October 1913, 57.

[2]) This tree has also been called Sydney peppermint in order to distinguish it from *E. amygdalina*, the white or brown peppermint tree.

[3]) Journ. and Proceed. Royal Soc. of N. S. W. 31 (1897), 195. — Research, p. 166. — See also Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 299.

phellandrene, pinene, cineol and a *sesquiterpene*. According to Baker and Smith the constants of the oil are as follows: $d_{18°}$ 0.9111; $[\alpha]_D$ — 2.97°; S. V. 11.0; it yields a clear solution with 1 vol. of 80 p. c. alcohol; $n_{D18°}$ 1.4838[1]).

For an oil derived from *Eucalyptus piperita* Wilkinson[2]) gives $d_{18°}$ 0.9133; $[\alpha]_{D18°}$ + 1.6°.

An oil prepared by Carthaus in the Tengger mountains, Java, from a species with long leaves (presumably *E. piperita*) had a golden-yellow color. Its constants were determined by Schimmel & Co.[3]): $d_{18°}$ 0.8974; α_D — 28° 26′; with 8 vol. of 80 p. c. alcohol it yielded a turbid solution. It contained *cuminic aldehyde* and much *phellandrene*. Finally Baker and Smith[4]) observed in connection with an oil possibly obtained from a variety of *E. piperita* the following constants: $d_{15°}$ 0.8785; α_D — 40.52°; S. V. 2.75; with 10 vol. of 80 p. c. alcohol is did not yield a clear solution.

632. Oil of Eucalyptus amygdalina.

Origin. Known as messmate, *Eucalyptus amygdalina*, Labill.[5]), which occurs in New South Wales, South Australia, Tasmania and Victoria, is one of the tallest of the eucalypts. According to F. v. Mueller it attains a hight of 400 ft. According to Baker and Smith the true *E. amygdalina* is found only in Tasmania. The *E. amygdalina* of the continent is to be regarded as *E. a.* var. *Australiana*, Baker et Smith. Their earlier opinion[6]) that the amygdalina oil of commerce is obtained from *E. amygdalina* var. *latifolia*, Deane et Maiden, is thus altered.

The leaves of *E. amygdalina* are richer in oil than those of any other species and yield up to 4.215 p. c. upon distillation. For a time large quantities were found in the market, but it has been replaced more and more by oils richer in cineol.

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[1]) Smith, *loc. cit.* 46.

[2]) Proceed. Royal Soc. of Victoria 1893, 198.

[3]) Report of Schimmel & Co. April 1909, 52.

[4]) Journ. and Proceed. Royal Soc. of N. S. W. 81 (1897), 195.—Research, p. 166.—See also Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 299.

[5]) Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 149. Maiden records 21 synonyms for this tree.

[6]) Chemist and Druggist 54 (1899), 864.

More recently large amounts of eucalyptus oil, more particularly of *E. amygdalina*, are finding use in the mining industry, especially in the production of zinc and lead sulphides. The washed or finely pulverized ores are mixed with an aqueous emulsion of eucalyptus oil. The oil takes up the fine particles of sulphide carrying them to the surface, at the same time taking along the particles of silver and gold contained in the ore. In 1911 the Barrier mines alone consumed 10 tons of oil per month[1].

Properties. The oil is of a light yellow color or colorless and has a faint odor of peppermint. For the oil distilled on the continent *(E. a.* var. *Australiana)* Baker and Smith[2] record the following constants: $d_{15°}$ 0.9012 and 0.9026; $[\alpha]_D$, — 11.37 and — 13.53; S. V. 3.76; S. V. after acetylation 22.4; cineol content 22 and 32 p.c.; soluble in $1^1/_2$ vol. of 70 p.c. alcohol; $n_{D16°}$ 1.4760[3]). The higher the specific gravity and the lower the angle of rotation, the richer the oil is in cineol and the poorer in phellandrene. The phellandrene reaction given below is characteristic for the oil. For Tasmanian oils Baker and Smith obtained the following constants: $d_{15°}$ 0.8668 to 0.8848; α_D, — 59.1 to — 75.1°; $n_{D18°}$ 1.4761 to 1.4790; S. V. 2.9 to 3.2; soluble in 7 vol. of 70 p.c. and in an equal vol. of 80 p.c. alcohol. Cineol content 12 to 24 p.c.

The amygdalina oil of commerce which, in all probability, is not a uniform product but a mixture of the distillates of several species, has a sp. gr. of 0.86 to 0.91 (15°) and is characterized, for the most part, by its incomplete solubility. Even of 90 p.c. alcohol several volumes are, as a rule, required for its solution which is not always clear.

Composition. According to O. Wallach and E. Gildemeister[4], the commercial oil of *Eucalyptus amygdalina* consists principally of l-*phellandrene*. If to a solution of the oil in two volumes of

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[1] Comp. Report of Schimmel & Co. April 1911, 72; October 1911, 49; April 1912, 79.

[2] Research, p. 168.—A research on the eucalypts of Tasmania, Hobart 1912, pp. 62, 64; Report of Schimmel & Co. October 1913, 58.

[3] Smith, *loc. cit.* 45.

[4] Liebig's Annalen 246 (1888), 278.

petroleum ether a concentrated aqueous solution of sodium nitrite and then acetic acid be added little by little, phellandrene nitrite is formed in such quantities that the entire liquid congeals to a pasty mass.

It is noteworthy that the phellandrene is lævogyrate and that this optical modification was first observed in connection with this oil.

Amygdalina oil contains but little *cineol*. Its detection cannot be accomplished by means of its hydrogen chloride addition product. The hydrogen bromide addition product, however, can readily be separated from the petroleum ether solution of the oil.

As already stated Baker and Smith found up to 32 p.c. of cineol in the oil, also small amounts of phellandrene and *pinene*. Of *eudesmol*, only traces could be detected. *Methyl, ethyl,* iso*butyl* and *amyl alcohols* were characterized by their oxidation to the corresponding acids or aldehydes. In the aqueous distillate they found *acetic acid* (barium salt)[1].

The Tasmanian oil from *Eucalyptus amygdalina* differs from the continental oil from *E. a.* var. *Australiana* by its lesser cineol content, its greater lævorotation, its higher phellandrene content and its more sparing solubility in alcohol. Its odor is also less aromatic.

633. Oil of Eucalyptus vitrea.

White top messmate, the *Eucalyptus vitrea,* R. T. Baker, is, according to Maiden[2]), a hybrid of *E. amygdalina* and *E. coriacea*. It is indigenous to a large part of New South Wales and Victoria. Baker and Smith[3]) obtained the oil with a yield of 1.48 p.c. The crude oil, which is almost colorless, has a fairly pleasant peppermint odor. It contains much *phellandrene,* little *cineol,* a *sesquiterpene,* small amounts of *piperitone* and probably *citral.* d_{15}. 0.886; $[\alpha]_D$ — 33.92; n_{D16}. 1.4828[4]); A. V. 1.1; E. V. 4.3; with an equal volume of 80 p.c. alcohol it yields a clear solution.

[1]) Research, p. 252.

[2]) A critical revision of the genus Eucalyptus, vol. I. p. 164.

[3]) Proceed. Linnean Soc. of N. S. W. 1900, 303. — Research, p. 176; Report of Schimmel & Co. October 1901, 28.

[4]) Smith, *loc. cit.* 46.

634. Oil of Eucalyptus Luehmanniana.

Eucalyptus Luehmanniana, F. v. M. is a rare species indigenous to New South Wales. From its leaves Baker and Smith[1]) obtained 0.289 p.c. of an amber-yellow oil with a peppermint-like odor. It contains much *phellandrene,* little *cineol, piperitone* and possibly *citral.* d_{15° 0.879; α_D —31.3°; n_{D16} 1.4937[2]); E.V. 2.3; with 10 vol. of 80 p.c. alcohol it does not yield a clear solution.

635. Oil of Eucalyptus campanulata.

To this group there probably also belongs the oil described by Baker and Smith[3]), which was obtained from *Eucalyptus campanulata,* Baker et Smith (bastard stringybark), a species that occurs in the northeastern part of New South Wales. The leaves yielded 0.851 p.c. of oil. The crude oil was light yellow in color; d_{15° 0.8804; α_D — 25.8'; n_{D18} 1.4856; S.V. 7.6; scarcely soluble in 10 vol. of 80 p.c. alcohol. The principal constituent is *phellandrene.* It also contains *cineol, piperitone* and *eudesmol.*

Group VI b.

Oils which consist principally of phellandrene and piperitone and which contain very little or no cineol.

636. Oil of Eucalyptus coriacea.

One of the mountain species, *Eucalyptus coriacea,* A. Cunn. (*E. pauciflora,* Sieb.) grows in a section of New South Wales, in Victoria, South Australia and Tasmania, where it is known as cabbage or white gum. Baker and Smith[4]) distilled the oil with a yield of 0.452 p.c. The light yellowish-brown crude oil has an odor of peppermint. It contains much *phellandrene* and *sesquiterpene,* a small amount of *cineol,* also *pinene* and *piperitone.* d_{15° 0.8947; $[\alpha]_D$ -- 32.8°; n_{D16} 1.4902[2]); A.V. 1.68; E.V. 2.94; soluble in an equal volume of 80 p.c. alcohol.

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[1]) Research, p. 177.—See also Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 287.

[2]) Smith, *loc. cit.* 46.

[3]) Journ. and Proceed. Royal Soc. of N.S.W. 45 (1911), 288; Report of Schimmel & Co. October 1912, 63.

[4]) Research, p. 179. See also Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 133.

For an oil from *Eucalyptus pauciflora,* Sieb. Wilkinson[1]) gives the following constants: d 0.8943 to 0.920; $[\alpha]_D$, + 6 to + 16.7°.

637. Oil of Eucalyptus Sieberiana.

Eucalyptus Sieberiana, F. v. M.[2]) (mountain ash) is a native of New South Wales, South Australia, Victoria and Tasmania. Its oil was distilled by Baker and Smith[3]) with a yield of 0.494 p.c. It is almost colorless and has an odor of peppermint. It consists for the most part of *phellandrene* and *piperitone.* $d_{15°}$ 0.88; $[\alpha]_D$ -- 48.8°; A. V. 0.65; E. V. 1.85; it does not yield a clear solution with 10 vol. of 80 p.c. alcohol.

In connection with an oil obtained from Sydney, Schimmel & Co. ascertained, the following properties; $d_{15°}$ 0.9087; α_D — 19° 36'; $n_{D18°}$ 1.4886[4]); not soluble in 10 vol. of 80 p.c. alcohol, soluble in 0.5 vol. of 90 p.c. alcohol, the solution becomes turbid upon the addition of 1.5 vol. and more. The oil reveals a decided phellandrene reaction.

638. Oil of Eucalyptus oreades.

Likewise known as mountain ash, *Eucalyptus oreades,* R. T. Baker (*E. virgata,* Sieb. var. *altior,* H. D. et J. H. M.), occurs in parts of New South Wales. Its oil (yield 1.16 p.c.) was described by Baker and Smith[5]) as an almost colorless liquid, with a peppermint odor, containing much phellandrene and small amounts of *piperitone* and *eudesmol.* $d_{15°}$ 0.8869; $[\alpha]_D$ — 25.6°; $n_{D18°}$ 1.4945[4]); A. V. 8.12; with an equal volume of 80 p.c. alcohol it forms a clear solution.

639. Oil of Eucalyptus dives.

Eucalyptus dives, Schau.[6]) is known as peppermint or broad-leaved peppermint. It occurs in Victoria and New South

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[1]) *Loc. cit.* p. 198.

[2]) Maiden, *loc. cit.* 306.

[3]) Research, p. 180.

[4]) Smith, *loc. cit.* 46.

[5]) Research, p. 181. — Proceed. Linnean Soc. of N. S. W. 1899, 596; Report of Schimmel & Co. October 1900, 32.

[6]) Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 190.

Wales. By v. Müller this species was regarded as synonymous with *E. amygdalina*. According to Baker and Smith[1]) it was because of this confusion that *E. amygdalina* acquired the reputation of yielding poor oil and wood. The oil is distilled with a yield of 1.962 to 2.89 p.c. It is an almost colorless liquid, the principal constituent of which is *phellandrene*. It also contains *piperitone*. $d_{15°}$ 0.882 to 0.8887; $[\alpha]_D$ - 62.68 to - 72.45°; $n_{D18°}$ 1.4894[2]); S.V. 0.29; E.V. 2.61; it is mostly soluble in 1 vol. of 80 p.c. alcohol, at times, however, it requires as much as 10 vol. for solution.

This oil, like many eucalyptus oils rich in phellandrene, contains a ketone $C_{10}H_{16}O$ for which Baker and Smith have suggested the name *piperitone*. In the pure state it has an intense odor of peppermint and imparts to many eucalyptus oils a peppermint-like odor. This explains why in Australia so many eucalypts are called peppermint. This substance can be separated from fractions boiling between 227 and 240° by shaking with bisulphite solution. It should be remembered, however, that piperitone reacts very slowly with bisulphite and that the shaking must be continued for some time. Piperitone boils between 224 and 225°; $d_{15°}$ 0.9393. Reduced with sodium and alcohol it yields a substance that melts at 155 to 156°, possibly an alcohol $C_{10}H_{18}O$, which probably occurs in small amounts in the oil.

Pharmacologically the oil has been examined by C. Hall[3]). It appears to possess strongly antiseptic properties.

640. Oil of Eucalyptus radiata.

Eucalyptus radiata, Sieb. (white-top peppermint, river white gum) occurs in most regions of New South Wales. It is frequently confounded with *E. amygdalina*. Baker and Smith[4]) obtained the oil with a yield of 1.22 to 1.88 p.c. The ·crude product is almost colorless and has an odor of peppermint.

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[1]) Research, p. 183.

[2]) Smith, *loc. cit.* 46.

[3]) On eucalyptus oils, especially in relation to their bactericidal power. Parramatta 1904; Report of Schimmel & Co. October 1904, 37.

[4]) Research, p. 185.

It consists very largely of *phellandrene*, also contains *pinene*, *cineol* and *piperitone*. d_{15° 0.8695 to 0.8747; $[\alpha]_D$ — 74.48 to - 89.4°; n_{D18} 1.4863[1]); A. V. 0.49; E. V. 2.8 and 3.88.

641. Oil of Eucalyptus Delegatensis.

White ash, silver-topped mountain ash, and gum-topped stringybark are common names applied to *Eucalyptus Delegatensis*, R. T. Baker *(E. gigantea, Hook. f. part.).* It inhabits the mountains of New South Wales and Victoria. According to Baker and Smith[2]), the oil (yield 1.3 to 1.9 p. c.) is a colorless liquid, of which *phellandrene* is the principal constituent. In addition it contains *piperitone* and a *sesquiterpene* but probably no cineol. d_{15} 0.8595 to 0.8664; α_D — 47.4 to — 58.6°; n_{D16° 1.4881[1]); S. V. 3.1 and 3.5; not soluble in 10 vol. of 80 p.c. alcohol.

642. Oil of Eucalyptus obliqua.

Eucalyptus obliqua, L'Hérit. *(E. gigantea,* Hook. f.[3]); *E. falcifolia,* Miq.: *E. nervosa,* F. v. M.)[4]) is one of the stringybarks and is distributed over the western part of Australia. Its oil was distilled by Baker and Smith[5]) with a yield of 0.66 to 0.77 p. c. *Phellandrene* is said to be the principal constituent; in addition it contains *aromadendral* and traces of *cineol.* d_{15° 0.8836 to 0.8902; α_D — 24.2 and — 28.8°; n_{D16° 1.4934[6]); S. V. 7.2 and 8.1; with 1 to 3 vol. of 80 p. c. alcohol it yields a clear solution.

An oil prepared in Portugal had the specific gravity 0.914; α_D — 7° 28′; soluble in the equal volume of 90 p.c. alcohol. It contained *cineol* and *phellandrene.*

[1]) Smith, *loc. cit.* 46.

[2]) Research, p. 186. — Proceed. Linnean Soc. of N. S. W. 1900, 305; Report of Schimmel & Co. October 1901, 28. — A research on the Eucalypts of Tasmania, Hobart 1912, p. 45; Report of Schimmel & Co. October 1918, 58.

[3]) According to Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 291, *E. gigantea* is a good species but has frequently been confounded with *E. obliqua.*

[4]) Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 51.

[5]) Research, p. 188. — A research on the Eucalypts of Tasmania, Hobart 1912, p. 50. See also Maiden, The useful native plants of Australia, p. 272. London and Sydney 1889.

[6]) Report of Schimmel & Co. October 1898, 26.

643. Oil of Eucalyptus gomphocephala.

Eucalyptus gomphocephala, D.C.[1]), a West Australian species, is called *touart* or *tooart* by the natives. The oil, which was obtained with a yield of 0.031 p. c., has been reported on by Baker and Smith[2]). In the crude state it is a reddish liquid, with an unpleasant rancid odor, consisting principally of terpenes, of which *phellandrene* is the principal representative. Cineol could not be found. $d_{15^\circ} 0.8759$; $n_D 1.4815$; E.V. 25.74; with 10 vol. of 80 p. c. alcohol it does not yield a clear solution.

644. Oil of Eucalyptus Andrewsi.

Formerly *Eucalyptus Andrewsi,* J. H. Maiden was regarded as a variety *(Oxleyensis)* of *E. Sieberiana,* but has been recognized as a separate species by Maiden[3]). The oil yield from leaves collected, according to Baker and Smith[4]), in the northeastern part of New South Wales was 1.27 p. c. $d_{15^\circ} 0.8646$, $\alpha_D - 41.5°$; $n_{D15°} 1.4854$; E.V. 4.3; insoluble in 10 vol. of 80 p. c. alcohol. The lemon-yellow crude oil consists mainly of *l-phellandrene* (m. p. of nitrite 105° and 112 to 113°), *piperitone* and a *sesquiterpene.* Pinene appears to be absent and the presence of *cineol* could scarcely be detected.

645. Oil of Eucalyptus taeniola.

To this group there possibly also belongs the oil of *Eucalyptus taeniola,* Baker et Smith[5]). The yield amounts to 0.66 p. c. It contains 7 p. c. *cineol* (resorcinol method), much *phellandrene,* also *eudesmol,* a *sesquiterpene* and *piperitone.* $d_{15°} 0.8864$; $\alpha_D - 27.6°$; $n_{D17°} 1.4872$; S.V. 3.2; soluble in 5 vol. of 80 p. c. alcohol.

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[1]) Maiden, A critical revision of the genus Eucalyptus, vol. III. p. 19.

[2]) Pharmaceutical Journ. 75 (1905), 384.

[3]) A critical revision of the genus Eucalyptus, vol. I. p. 195.

[4]) Journ. and Proceed. Royal Soc. of N. S. W. 45 (1911), 273; Report of Schimmel & Co. October 1912, 63.

[5]) A research on the Eucalypts of Tasmania, Hobart 1912; p. 60; Report of Schimmel & Co. October 1913, 58.

Group VII.

This group comprises all oils that could not be classified with the other groups.

646. Oil of Eucalyptus stellulata.

Eucalyptus stellulata, Sieb.[1]) (lead gum, black Sally) grows in New South Wales and Victoria. It yields 0.293 p. c. of an amber-yellow oil to which Baker and Smith[2]) assign the following properties: $d_{15°}$ 0.871; $[\alpha]_D$ — 26.1°; $n_{D16°}$ 1.4902[3]); soluble in 10 vol. of 80 p. c. alcohol. It contains *phellandrene, sesquiterpene* and traces of *cineol*.

647. Oil of Eucalyptus Macarthuri.

In the moist regions of New South Wales there grows *Eucalyptus Macarthuri*, Deane et Maiden, known as Paddy's river box and Camden woolly-butt. The oil, yield 0.112 p. c., was first described by Baker and Smith[4]). Its principal constituent is *geranyl acetate*. Furthermore it contains *eudesmol*, possibly *pinene* and free *geraniol* (characterized by its oxidation to citral). Baker and Smith record the following properties: $d_{15°}$ 0.9218 to 0.9245; $[\alpha]_D$ + 1.2 to + 3.89°; $n_{D16°}$ 1.4793[3]); E. V. 171.3 to 214 (= 60 to 75 p. c. of geranyl acetate); soluble in $1^1/_2$ vol. of 70 p. c. alcohol. For the crude oil Schimmel & Co.[5]) report the following properties: $d_{15°}$ 0.9225; α_D + 1° 15′; S. V. 204.8 (= 71.68 p. c. of geranyl acetate); E. V. after acetylation 240 (= 80.5 p. c. $C_{10}H_{18}O$). For the rectified oil: $d_{15°}$ 0.9175; α_D 0° 21′; S. V. 211.3 (= 73.95 p. c. geranyl acetate); E. V. after acetylation 244.2 (= 82.2 p. c. $C_{10}H_{18}O$). The rectified oil was of a dark lemon-yellow color and yielded a clear solution with 4 vol. and more of 70 p. c. alcohol. During the process of rectification the bulk of the odorless eudesmol

[1]) Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 127.

[2]) Research, p. 190.

[3]) Smith, *loc. cit.* 47.

[4]) Research, p. 191, 212, 234. — Journ. and Proceed. Royal Soc. of N. S. W. 84 (1900), 142; Report of Schimmel & Co. April 1901, 34.

[5]) Report of Schimmel & Co. April 1902, 38.

remains behind. Schimmel & Co.[1]) also demonstrated the presence of geraniol by its oxidation to citral.

648. Oil of Eucalyptus aggregata.

Black gum, *Eucalyptus aggregata,* Deane et Maiden, grows in the swampy regions of New South Wales. Baker and Smith[2]) distilled the oil with a yield of 0.04 p. c. and described it as a light orange-brown liquid possessing the following properties: $d_{15°}$ 0.956; $[\alpha]_D + 27.13°$; $n_{D16°}$ 1.5062[2]); E. V. 112.2; it does not yield a clear solution with 10 vol. of 80 p. c. alcohol. It contained relatively much d-*α-pinene* (characterized by its nitrosochloride), no phellandrene or cineol, but *eudesmic acid amyl ester* as principal constituent. Free eudesmic acid (from *Eudesmia* as Robert Brown had named the genus *Eucalyptus*) constitutes white, rhombic prisms, which melt at 160°. It is an unsaturated mono-basic acid of the formula $C_{14}H_{18}O_2$ and yields a dibromide which melts at 102 to 103°. Nothing is known as to its chemical nature; it may belong to the cinnamic acid group. The amyl alcohol was characterized by its oxidation to valeric acid. Eudesmic acid amyl ester appears to be present in numerous eucalyptus oils. The amyl alcohol found by Bouchardat and Oliviero in the oil of *E. Globulus* presumably owes its origin to the decomposition of this ester.

649. Oil of Eucalyptus virgata.

The oil of *Eucalyptus virgata,* Sieb., ironbark, is one of the most peculiar eucalyptus oils. It contains so much *eudesmol* that it frequently congeals in the condenser while being distilled[4]). In addition it contains an appreciable amount of l-*phellandrene* and about 21 p. c. of *cineol* (resorcinol method). $d_{15°}$ 0.8883 and 0.9154; $\alpha_D - 20.9$ and $- 35.8°$; $n_{D16°}$ 1.5015[3]); S. V. 3.3 and 5.76; with 1 to 3 vol. of 80 p. c. alcohol it yields a clear solution. The yield amounts to about 0.79 p. c.

[1]) Report of Schimmel & Co. April 1901, 34.

[2]) Research, p. 193, 225. — Journ. and Proceed. Royal Soc. of N. S. W. 34 (1900), 72; Report of Schimmel & Co. April 1901, 33.

[3]) Smith, *loc. cit.* 47.

[4]) Research, p. 194, 212. — A research on the Eucalypts of Tasmania, Hobart 1912, p. 56. — See also Maiden, A critical revision of the genus eucalyptus, vol. I. p. 273.

650. Oil of Eucalyptus patentinervis.

Bastard mahogany, *Eucalyptus patentinervis*, R. T. Baker, occurs in New South Wales. Baker and Smith[1]) obtained the oil with a yield of 0.254 p.c. It contains *citral* (characterized by its naphthocinchoninic acid), a *sesquiterpene,* and possibly limonene. d_{15° 0.8735; $[\alpha]_D$ - 17.4°; n_{D16° 1.4948[2]); A.V. 2.46; E.V. 3.74; S.V. after acetylation 63.3; it does not yield a clear solution with 10 vol. of 80 p.c. alcohol.

651. Oil of Eucalyptus apiculata.

One of the shrubby eucalypts of New South Wales is *Eucalyptus apiculata,* Baker et Smith. The leaf oil was distilled by Baker and Smith[3]) with a yield of 0.65 p.c., which in the crude condition is of an orange-brown color. It consisted of *pinene, piperitone,* and a small amount of *cineol.* d_{15° 0.9056 and 0.9112; $[\alpha]_D$ 8.56 and 9.27°; n_{D16° 1.4934[2]); S.V. 8.7 and 10.05; E.V. after acetylation 39.74; it yields a clear solution with an equal volume of 80 p.c. alcohol.

652. Oil of Eucalyptus citriodora.

Formerly *Eucalyptus citriodora,* Hook. was regarded as a variety of *Eucalyptus maculata,* however, according to Baker and Smith[4]) it is a distinct species. The tree, which is indigenous to Queensland, prefers a rocky soil. It has been cultivated with success in Zanzibar and along the Magdalen river[5]).

The oil, which is characterized by its agreeable citronella-like odor, is used extensively in perfumery. According to Baker and Smith it is obtained with a yield of 0.586 p.c. The crude oil had the following constants: d 0.864; $[\alpha]_D$ — 1.15°; n_{D16° 1.4651 to 1.4678[6]); S.V. 7.5; soluble in 1.5 vol. of 70 p.c. alcohol. For commercial oils Schimmel & Co[7].) recorded the following

[1]) Research, p. 196.

[2]) Smith, *loc. cit.* 46.

[3]) Research, p. 198. See also Maiden, A critical revision of the genus Eucalyptus, vol. I. p. 285.

[4]) Research, p. 199.

[5]) v. Müller, Select extra-tropical plants, IX. ed. Melbourne 1895, p. 187.

[6]) Smith, *loc. cit.* 47.

[7]) Report of Schimmel & Co. April 1901, 35; October 1907, 51.

data: $d_{18°}$ 0.870 to 0.905; α_D inactive or slightly dextrogyrate, to $+ 2°$[1]); $n_{D20°}$ 1.454 to 1.461; soluble in 1 to 1.5 vol. and more of 80 p.c. alcohol, occasionally with slight opalescence. Some oils are soluble in 4 to 6 vol. of 70 p.c. alcohol. An East Indian product[2]) possessed very similar properties: $d_{15°}$ 0.8686; $\alpha_D + 0°20'$; soluble in 5 vol. and more of 70 p.c. alcohol. *Citronellal* is the principal constituent. It also contains small amounts of *pinene*, but neither phellandrene nor cineol. Baker and Smith found 91 p.c. of citronellal. After acetylation for one hour, Schimmel & Co. found 80 to 92 p.c.; acetylation for two hours[3]) yielded up to 98.5 p.c. of acetylizable constituents.

In the Imperial Institute of London[4]) the following constants were ascertained in connection with two samples of *Eucalyptus citriodora* oils from Mauritius: $d_{16°}$ 0.877 and 0.879; $\alpha_{D21°} + 0°4'$ and $+1°16'$; soluble in 3 and 2.6 vol. of 70 p.c. alcohol. The assay of acetylizable constituents yielded 81.1 and 87.1 p.c. Both oils had a strong odor of citronellal.

653. Oil of Eucalyptus marginata.

From the young leaves of *jarrah*, by which name *Eucalyptus marginata*, Sm. is known in southwestern Australia, Baker and Smith[5]) obtained 0.20 p.c. of oil, and from the older leaves 0.24 p.c. The former revealed the following properties: $d_{18°}$0.8889; α_D 10.4°; $n_{D16°}$1.4946; the latter $d_{15°}$ 0.9117; $\alpha_D - 8.5°$; $n_{D16°}$1,4946; soluble in 1 to 5 vol. of 80 p.c. alcohol. Phellandrene was not found. *Pinene* and *cineol* were present in small amounts. In addition the oil contained *cymene*, a *sesquiterpene* and *aromadendral*, which was characterized by means of its oxime. The high boiling constituents of the oil revealed a blue color.

654. Oil of Eucalyptus salubris.

Gimlet gum, *Eucalyptus salubris*, F. v. M., is one of the most stately of forest trees in western Australia. Baker and

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[1]) An oil obtained by the firm *via* London (Report of Schimmel & Co. April 1901, 35) was noteworthy because of its strong laevorotation, $\alpha_D - 15°52'$.

[2]) Report of Schimmel & Co. October 1907, 51.

[3]) Comp. vol. I. p. 579.

[4]) Bull. Imp. Inst. 11 (1913), 48.

[5]) Pharmaceutical Journ. 75 (1905), 383.

Smith[1]) distilled its oil with a yield of 1.391 p.c. It possessed a strong odor of aromadendral. $d_{15°}$ 0.902; α_D —5.8°; $n_{D16°}$ 1.4841; S. V. 18.88; in 10 vol. of 70 p.c. the oil was insoluble, but it dissolved in 1 vol. of 80 p.c. alcohol. It is fairly rich in high boiling constituents, only 66 p.c. distilling over below 183°. The fraction distilling above 214' was rich in *aromadendral*. Other constituents found in the oil are d-*pinene, cymene, eucalyptol* (about 10 p.c.) and *esters*, presumably *geranyl acetate* for the most part. Its lævorotation the oil owes to the presence of aromadendral.

655. Oil of Eucalyptus Staigeriana.

The leaves of the lemon-scented iron bark, *Eucalyptus Staigeriana*, F. v. M. contain from 2.75 to 3.36 p.c. of an oil with a pleasant odor of lemon and verbena, for which Schimmel & Co.[2]) record a density of from 0.880 to 0.901. Baker and Smith[3]) record the following properties for the crude oil, which they distilled with a yield of 2.5 p.c.; $d_{16°}$ 0.8708; α_D —43.1°; $n_{D18°}$ 1.4871; insoluble in 6 vol. of 80 p.c. alcohol. The oil contains about 60 p.c. l-*limonene* (m. p. of tetrabromide 104 to 105°), 13 p.c. geraniol (?), 8 p.c. geranyl acetate (?) and 16 p.c. *citral.*

656. Oil of Eucalyptus Thozetiana.

According to Baker[4]) the *Lignum vitæ, Eucalyptus Thozetiana*, F. v. M. affords but an exceedingly small yield of oil. The very mobile product ($d_{15°}$ 0.9257; $n_{D18°}$ 1.5026) probably consists for the most part of saponifiable products.

657. Oil of Eucalyptus odorata.

Eucalyptus odorata, Behr (box-tree, peppermint gum-tree) is a tree distributed over South Australia, Victoria and New South Wales. According to Maiden[5]) the fresh leaves yield

[1]) Pharmaceutical Journ. 75 (1905), 358.

[2]) Bericht von Schimmel & Co. April 1888, 20.

[3]) Pharmaceutical Journ. 76 (1906), 571. Comp. Maiden, A critical revision of the genus Eucalyptus, vol. II. p. 69.

[4]) Proceed. Linnean Soc. of N. S. W. 1906, 305; Report of Schimmel & Co April 1907, 52.

[5]) The useful native plants of Australia, p. 272.

1.4 p.c. of oil. According to Baker and Smith[1]) the yield is not so high.

Properties. d 0.899 to 0.922; b. p. 157 to 199° (Maiden *loc. cit.*); d 0.9042; $[\alpha]_D + 2.43°$; S. V. 3.41; soluble in an equal volume of 80 p.c. alcohol (Baker and Smith); $n_{D18°} 1.4775$[2]; $d_{16°} 0.903$ (crude oil) and $d_{18°} 0.909$ (rectified oil)[3]).

Composition. Frequently the oil is so rich in *cineol* (identified by means of its hydrogen bromide addition product), that it congeals to a solid mass in a freezing mixture. From the rectification residue Schimmel & Co.[3]) isolated large amounts of *cuminic aldehyde* by means of its bisulphite compound. For purpose of identification it was oxidized to cuminic acid. According to Baker and Smith *(loc. cit.)* this was not cuminic aldehyde but aromadendral. However, Schimmel & Co. have proven by later investigations that cuminic aldehyde occurs in eucalyptus oils. (See oil of *Eucalyptus hemiphloia*, p. 265.) It is probable, therefore, that in addition to the cuminic aldehyde, the presence of which has been definitely established, aromadendral, which has a similar odor, is likewise present. d-*Pinene* is also a constituent of the oil. In commercial oils Schimmel & Co. occasionally observed decided reactions for *phellandrene*.

658. Oil of Eucalyptus Baileyana.

Another stringybark, *Eucalyptus Baileyana*, F. v. M.[4]) occurs in New South Wales and Queensland. Upon distillation the fresh leaves yield 0.9 p.c. of oil; b. p. 160 to 185°; d 0.940. It contains about 30 p.c. *cineol*.

659. Oil of Eucalyptus Loxophleba.

On account of its frequent occurrence in the vicinity of York, *Eucalyptus Loxophleba*, Benth.[5]) is popularly known as York

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[1]) Research, p. 211.

[2]) Smith, *loc. cit.* 45.

[3]) Bericht von Schimmel & Co. April 1889, 19.

[4]) Maiden, The useful native plants of Australia, p. 266; Bericht von Schimmel & Co. April 1888, 19. — See also Research, p. 202.

[5]) E. J. Parry, Pharmaceutical Journ. 61 (1898), 198. The paper gives Toxophleba instead of Loxophleba.

gum. This oil has an exceedingly disagreeable odor and irritates the mucous membranes causing coughing. $d_{15.5°}$ 0.8828; α_D abt. $+ 5°$. It contains *phellandrene* and *cineol*. The amount of the latter is estimated at about 15 to 20 p.c. When shaken with bisulphite the oil lost 20 p.c. of its volume, thus indicating considerable amounts of aldehydes and ketones. Amyl alcohol, small amounts of which are present in the oil of *Eucalyptus Globulus,* and to which its irritating action is due in part, is not present.

660. Oil of Angophora lanceolata.

From the leaves of *Angophora lanceolata,* Car. (family *Myrtaceæ*) Baker and Smith[1]) obtained 0.09 p.c. of oil in which they proved the presence of *aromadendrene* by means of the color reaction with bromine.

661. Oil of Leptospermum scoparium.

The oil of *Leptospermum scoparium,* Forst. (family *Myrtaceæ*), known as *manuka* by the natives of New Zealand, is described by C. E. Atkinson[2]) as a brown liquid of an aromatic odor and an astringent taste. $d_{12°}$ 0.916; congealing point $-17°$. It boils between 223 and 280°, for the most part about 260°.

662. Oil of Leptospermum Liversidgei.

The oil of *Leptospermum Liversidgei,* Baker et Smith has been distilled by Baker and Smith[3]). The crude oil was insoluble in 10 vol. of 70 p.c. alcohol, soluble in 1 vol. of 80 p.c. alcohol; $d_{15°}$ 0.8895; $\alpha_D + 9.2°$; $n_{D16°}$ 1.4903. At 170° 20 p.c. of the oil distilled over ($d_{15°}$ 0.8624; $\alpha_D + 32.5°$; $n_{D16°}$ 1.4774), between 195 and 225° 30 p.c. ($d_{15°}$ 0.8892; $\alpha_D + 5.7°$; $n_{D16°}$ 1.4892). The principal constituents are *citral* (35.0 p.c.; m.p. of naphthocinchoninic acid 199°), *geraniol* (9.74 p.c.), *geranyl acetate* (5.35 p.c.) and d-*pinene* (25 p.c.; m.p. of nitrosochloride 103°), a *sesquiterpene* (24.91 p.c.; $d_{16°}$ 0.9024; $n_{D16°}$ 1.5052). Limonene and phellandrene were not found.

[1]) Research, p. 248, 274.

[2]) Pharmaceutical Journ. 69 (1902), 369.

[3]) Journ. and Proceed. Royal Roc. of N. S. W. 39 (1905), 124; Report of Schimmel & Co. October 1906, 45.

663. Cajuput Oil.

Oleum Cajeputi. — Cajeputöl. — Essence de Cajeput.

Origin and Production. Cajuput oil is distilled from the fresh leaves and twigs of several species of *Melaleuca*, family *Myrtaceæ*, more particularly those of *M. Leucadendron*, L. and the variety known as *M. minor* (*M. Cajeputi*, Roxb., *M. viridiflora*, Gaertn.) These trees which attain a height of 15 m. are indigenous to Farther India, the islands of the Indian Ocean, northern Australia, Queensland and New South Wales.
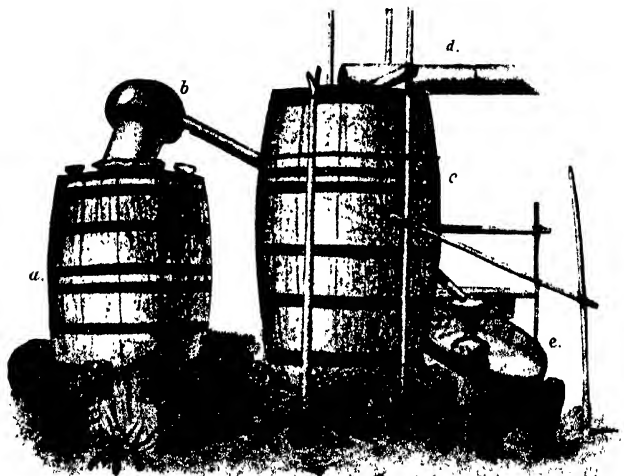
Fig. 22. Distillation of cajuput oil in Ceram (Moluccas).

In some of the Moluccas, cajuput oil is distilled in a primitive way by the natives. According to C. G. C. Reinwardt[1]) the oil was formerly distilled only in the island of Buru. In 1821 there were but three stills in the island, in 1855 there were as many as 50. More recently this industry has developed in Ceram. Martin[2]), who on his trip to the Moluccas during 1891 and 1892

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[1]) Reinwardt's *Reis naar het oostelijk gedeelte van den Indischen Archipel in het jaar* 1821. Amsterdam 1858, p. 473.

[2]) K. Martin, *Reisen in den Molukken*. Leiden 1894, p. 259.

visited Ceram and Buru described the method of production which is illustrated by the accompanying cut: —

"On a fireplace of crude masonry there stands a barrel one meter in height (fig. 22 a) which serves as still. Into it are pressed the leaves of the *Melaleuca* and the barrel is then half filled with water. The helmet *(b)*, which the distillers obtain from Ambon or Java, is placed on top and the beak ends in a second, somewhat larger barrel *(c)* which serves as a cooler. The latter is supplied with water from the slope of a neighboring hill by means of a bamboo tube *(d)*. The volatile oil of the plant passes over with the water vapor and separates upon cooling. Both oil and water flow into a funnel made of a cocoanut shell and thence into a bottle. Quadrangular brandy bottles, such as one meets everywhere in the East Indies are commonly used. At the base this bottle is provided with a small opening and is placed in a tub *(e)* so that at the beginning of the operation it is filled with water. The products of distillation, however, gradually displace the water in the flask, and the water that comes over with the oil likewise flows out of the opening at the bottom until the flask is completely filled with oil. This is then removed, the opening at the bottom being closed with the finger. With such an equipment the daily output amounts to about $1^{1}/_{2}$ liters. As is well-known the light blueish-green liquid is esteemed in Europe as volatile irritant, in Buru it is used as domestic remedy for all imaginable ailments."

This oil is transferred to empty wine and beer bottles, 25 of which are packed into a case made from the leaf stalks of the sago palm[1] *(Metroxylon)*. The exhausted cajuput leaves are used as packing. The principal point of collection for cajuput oil is Macassar in Celebes.

Production and Commerce. According to the statistics of this port[2], the total export of cajuput oil from Macassar was as follows: —

[1] An illustration of such an original package may be found in Tschirch's *Indische Heil- und Nutzpflanzen*. Berlin 1892. Plate 75 a. p. 127.

[2] In recent years the official lists of exports from Macassar no longer enumerate cajuput oil. The figures for 1911 and 1912 are taken from the Report of the British Vice-Consul. Report of Schimmel & Co. April 1908, 19; October 1910, 23; October 1911, 24; October 1913, 29.

1905	. .	3935 baskets[1])	1909	. .	1488 baskets
1906	. .	3713 „	1910	. .	1739˙ „
1907	. .	3695 „	1911	. .	2007 „
1908	. .	2950 „	1912	. .	2579 „ •

Statistics do not include the amounts of cajuput oil shipped directly from Buru island to Europe, mostly in iron drums.

Formerly the bulk of this oil was shipped via Java and Singapore to British India and only small amounts reached the European market via Amsterdam, Hamburg and London. More recently most of the oil has been shipped to the United States where it does not appear to have lost any of its former popularity.

Properties. Crude cajuput oil is colored green to blueish-green by copper, whereas the rectified oil is colorless or yellowish. It has the agreeable, camphor-like odor of cineol and an aromatic, somewhat burning, and afterward cooling, taste. $d_{15°} 0.919$ to 0.930; α_D slightly lævogyrate to $-3°40'$; $n_{D20°} 1.466$ to 1.471. Soluble in 1 volume and more of 80 p. c. alcohol, occasionally soluble in 2.5 to 3 vol. of 70 p. c. alcohol.

In a freezing bath of solid carbon dioxide and ether this oil congeals to a solid mass. The copper can be removed from the oil by shaking it with a concentrated aqueous solution of tartaric acid but not with water. H. C. Prinsen-Geerligs[2]) attributes this behavior to the presence of small amounts of butyric and valeric acids, free and as esters, which hold the copper in solution. As shown by its spectroscopic behavior, the crude oil contains chlorophyllane[3]), oxidized chlorophyll, in addition to copper.

In addition cajuput oil occasionally contains a high-boiling blue fraction.

Adulteration of cajuput oil with cocoanut oil[4]), petroleum[4])[5]) and eucalyptus oil[5])[6]) has been observed.

[1]) A basket contains 25 bottles, of about 600 g. net weight = abt. 15 kg. Baskets with a net weight of 30 kg. occur but they receive no special consideration in the statistics. Report of Schimmel & Co. April 1911, 25.

[2]) Chem. Weekblad 1 (1904), 931; Chem. Zentralbl. 1905, I. 95.

[3]) W. A. Tichomirov, Pharm. Zeitschr. f. Russl. 27 (1888), 548; Jahresb. f. Pharm. 1888, 317.

[4]) A. G. Vorderman, Rev. intern. falsific. 12 (1899), 146; Chem. Zentralbl. 1899, II. 970.

[5]) J. C. Umney, Chemist and Druggist 63 (1903), 725.

[6]) E. J. Parry, *ibidem* 783.

Composition. The earliest chemical investigations of cajuput oil were restricted to its principal constituent, $C_{10}H_{18}O$, the elementary composition of which was correctly ascertained by R. Blanchet[1]) in 1833. M. Schmidt[2]) named it cajuputene.hydrate, J. H. Gladstone[3]) also C. R. A. Wright and Lambert[4]) cajuputol. Its identity with *cineol* was established by O. Wallach[5]) by the preparation of its halogen and hydrohalogen addition products. Further proof was supplied by Wallach and E. Gildemeister[6]) by oxidation of the proper fraction to cineolic acid, $C_{10}H_{16}O_5$, which melts at 196 to 197°.

Second in importance as to quantity is the inactive *α-terpineol*, m. p. 35°, which was found in cajuput oil by R. Voiry[7]). It occurs free as well as acetic ester.

Of terpenes the oil contains but little. The lævogyrate fraction 155 to 165° yields a solid, lævogyrate monohydrochloride $C_{10}H_{16}HCl$[8]) that melts at 120 to 128°. Hence it consists in part at least of l-*α-pinene*.

The lowest fractions contain aldehydes. Upon separation with sodium acid sulphite, Voiry obtained a liquid that had the properties of *valeric aldehyde*. A second aldehyde that had the odor of bitter almond oil is probably *benzaldehyde*.

664. Niaouli Oil.

Origin and Production. The niaouli tree, *Melaleuca viridiflora*, de Brongn. et Gris. (family *Myrtaceæ*) is characteristic of very large areas of New Caledonia. This niaouli forest extends between pasture land and primitive forest to an altitude of 300 m. The oil is distilled from the fresh leaves with a yield of 2.5 p. c. in a number of establishments around Gomen, hence the designation gomenol[9]) that is customary in France.

[1]) Liebig's Annalen 7 (1833), 161.
[2]) Journ. Chem. Soc. 14 (1862), 63. — Journ. f. prakt. Chem. 82 (1861), 189.
[3]) Journ. Chem. Soc. 25 (1872), 1 *et seq.* — Pharmaceutical Journ. III. 2 (1872), 746. — Jahresber. d. Chem. 1872, 815.
[4]) Berl. Berichte 7 (1874), 598. — Pharmaceutical Journ. III. 5 (1874), 234.
[5]) Liebig's Annalen 225 (1884), 315.
[6]) *Ibidem* 246 (1888), 276.
[7]) Compt. rend. 106 (1888), 1538. — Bull. Soc. chim. II. 50 (1888), 108. — Journ. de Pharm. V. 18 (1888), 149.
[8]) Report of Schimmel & Co. April 1892, 10.
[9]) Bullet. Gén. de Thérap. 136, 1; Pharmaceutical Journ. 61 (1898), 241.

Properties. In its properties and composition niaouli oil closely resembles cajuput oil: $d_{15°}$ 0.908 to 0.929; α_D slightly dextrogyrate or (for the most part) lævogyrate; $n_{D20°}$ 1.47225 (1 determination); A. V. 1.3; E. V. 7.4 (1 determination); soluble in about 1 vol. of 80 p. c. alcohol; of 70 p. c. alcohol it required from 4 to 25 vol. to effect a clear solution.

Composition[1]). In place of l-α-pinene found in cajuput oil, niaouli oil contains d-α-*pinene* from which a solid monohydrochloride $C_{10}H_{16}HCl$ was prepared. *Cineol* (35 to 60 p. c.) is the principal constituent and is accompanied by a lævogyrate substance of the same boiling point (*l*-limonene?). About 30 p. c. of the oil is composed of crystallizable α-*terpineol* (m. p. 35°) and its *valeric* ester. In addition, traces of *acetic* and *butyric* acid esters are present. With sodium acid sulphite solution Bertrand removed two aldehydes from the oil. One of these had the odor of valeric aldehyde, the other that of bitter almond and boiled at 180° (benzaldehyde?). The unpleasant odor of the crude oil is due to sulphur compounds.

665. Oil of Melaleuca acuminata.

The leaves of *Melaleuca acuminata*, F. v. Müll. yield a colorless oil with an odor reminding faintly of juniper berries. d 0.892; α_D — 15° 20'. It contains much *cineol*[2]).

666. Oil of Melaleuca bracteata.

The oil of *Melaleuca bracteata*, F. v. Müll. was distilled from the leaves and twigs by R. T. Baker and H. G. Smith[3]) with a yield of 0.643 to 0.964 p. c. and revealed the following constants: $d_{18°}$ 1.032 to $d_{19°}$ 1.0358; α_D — 1.4 to — 3.1°; $n_{D20°}$ 1.5325 to 1.535; A. V. 0.7 to 1.26; S. V. 5.3 to 20.8; E. V. of the saponified oil after acetylation 24.57; soluble in 0.7 to 0.8 vol. of 70 p. c. alcohol. It contains 0.36 p. c. of *eugenol* (m. p. of the benzoyl compound

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[1]) G. Bertrand, Bull. Soc. chim. III. 9 (1893), 432; Compt. rend. 116 (193), 1070. — R. Voiry, Contribution à l'étude chimique des huiles essentielles de quelques Myrtacées. Thése de l'Ecole supérieure de Pharmacie de Paris 1888.

[2]) Report of Schimmel & Co. April 1892, 60.

[3]) Journ. and Proceed. Royal Soc. of N. S. W. 44 (1911), 601; Report of Schimmel & Co. April 1912, 93.

68 to 69°); 0.33 p. c. free *cinnamic acid,* also combined cinnamic acid (m. p. 133°), traces of *cinnamic aldehyde,* little l-*phellandrene* (m. p. of the nitrite 120°), *cinnamyl cinnamate* (?) and 70 p. c. *methyl eugenol* (Zeisel determination), which was characterized by its bromide, m. p. 77 to 78° and by its oxidation to veratric acid melting at 178 to 179°.

A sample examined by Schimmel & Co.[1]) was light yellow in color and had a pleasant odor reminding somewhat of champaca oil. $d_{15°}$ 1.0422; α_D — 1°10'; $n_{D20°}$ 1.53428; A. V. 0.4; E. V. 20.8; E. V. after acetylation 31.0; soluble in 1.5 vol. and more of 70 p. c. alcohol.

667. Oil of Melaleuca decussata.

The leaves and twigs of *Melaleuca decussata,* R. Br. yield upon distillation 0.037 p. c. of oil; d 0.938; b. p. 185 to 209°. Odor and taste are very similar to those of cajuput oil[2]).

668. Oil of Melaleuca ericifolia.

The leaves of *Melaleuca ericifolia,* Sm. yield 0.033 p. c. of oil which, likewise, resembles the oil of cajuput. d 0.899 to 0.902. It boils between 149 and 184°[1]), is dextrogyrate[3]) and contains *cineol.*

669. Oil of Melaleuca genistifolia.

According to Bosisto, *Melaleuca genistifolia,* Sm. contains 0.07 p. c. of oil. From the leaves and twigs, which had been collected along the coast of New South Wales, Baker and Smith[4]) obtained 0.526 p. c. of an oil of a light yellow color which had a decided odor of turpentine oil; $d_{15°}$ 0.8807; α_D + 32.7; $n_{D22°}$ 1.4702; S. V. 6.8; insoluble in 10 vol. of 80 p. c. alcohol. In fraction 154 to 158° the presence of d-α-*pinene* (80 to 90 p. c.; m. p. of nitroso-chloride 104°) was demonstrated. Fraction 162 to 183° contained

[1]) Journ. and Proceed. Royal Soc. of N. S. W. 44 (1911), 601; Report of Schimmel & Co. April 1912, 93.

[2]) J. H. Maiden, The useful native plants of Australia. London and Sydney, 1889, p. 275.

[3]) J. H. Gladstone, Journ. chem. Soc. 25 (1872), 1 *et seq.;* Pharmaceutical Journ. III. 2 (1872), 746; Jahresber. d. Chem. 1872, 815.

[4]) Journ. and Proceed. Royal Soc. of N. S. W. 45 (1911), 365; Report of Schimmel & Co. October 1912, 81.

cineol (2 p. c. computed with reference to the original oil; resorcinol method). The highest fractions contain a *sesquiterpene*.

670. Oil of Melaleuca gibbosa.

The material distilled by Baker and Smith[1] consisted of leaves and twigs of *Melaleuca gibbosa,* Labill. that had been collected in Tasmania. The yield was 0.158 p. c. The crude oil was dark yellow and had an odor of cineol and pinene: $d_{15°} 0.9138$; $\alpha_D + 4.5$; $n_{D20°} 1.4703$; S. V. 9.9; insoluble in 10 vol. of 70 p. c. alcohol, soluble in an equal volume of 80 p. c. alcohol. 61,5 p. c. of the oil consisted of *cineol* (resorcinol method). Another important constituent is d-*α-pinene* (m. p. of nitrosochloride 104°). The high boiling fractions contain a *sesquiterpene* and probably terpinyl acetate.

671. Oil of Melaleuca Leucadendron var. lancifolia.

Melaleuca leucadendron, L., the parent plant of cajuput oil, occurs all over Australia and the Malay territory. According to R. C. Cowley[2] seven varieties occur in Queensland. One variety, *M. L.* var. *lancifolia* known as tea-tree[3]) in the Brisbane district, is a tree 20 ft. high with leaves about 8 cm. long. The yield of oil is said to be poor (the percentage is not recorded by the author). It has the following properties: d 0.922; $\alpha - 3°$; n 1.4623. The colorless oil has a decided odor of cajuput oil and contains 45 p. c. *cineol* (the assay method is not given).

An oil previously examined by Schimmel & Co.[4] consisted largely of cineol; $d_{15°} 0.955$; $\alpha_D - 3° 38'$.

672. Oil of Melaleuca linariifolia.

From the leaves and twigs of *Melaleuca linariifolia,* Sm. distilled in September, Baker and Smith[5] obtained 1.214 p. c. of oil. The crude oil was light yellow and had a turpentiny

[1]) *Loc. cit.* 369.

[2]) Chemist and Druggist 76 (1910), 832.

[3]) According to Baker and Smith, the Melaleucas are quite generally designated as "Tea-tree".

[4]) Report of Schimmel & Co. April 1892, 60.

[5]) Journ. and Proceed. Royal Soc. of N. S. W. 40 (1906), 65; Report of Schimmel & Co. April 1907, 14.

odor. $d_{15°}$ 0.9129; $\alpha_{D} + 2.5°$; n_{D22} 1.4741; S.V. 6.4; E.V. after acetylation 40.3; insoluble in 10 vol. of 70 p.c. alcohol, soluble in 1 vol. of 80 p.c. alcohol, 10 vol. cause slight turbidity.

Upon fractionation 52 p.c. passed over between 175 and 183′, an additional 23 p.c. up to 250′. The oil contains neither pinene nor phellandrene. The *cineol* content is small. The lowest fractions contained small amounts of aldehydes. The *alcohol* contained in the oil appears to be identical with that found in *M. thymifolia*. The high-boiling portions contain a *sesquiterpene*.

Schimmel & Co.[1]) have had occasion to investigate a color-less distillate of a peculiar aromatic odor; $d_{15°}$ 0.9109; $\alpha_{D} + 3°$; soluble in 1.5 vol. of 80 p.c. alcohol, the addition of more than 3 vol. causes opalescence. It contains appreciable amounts of *cineol*. Aqueous acid sulphite solution extracted an *aldehyde* which presumably is identical with citronellal. The amount of available oil was too small to admit of chemical identification.

673. Oil of Melaleuca nodosa.

From leaves and twigs of *Melaleuca nodosa*, Sm. collected about the middle of June, Baker and Smith[2]) obtained 0.664 p.c. of volatile oil. The crude product was lemon-yellow and possessed a turpentiny odor which was somewhat covered by small amounts of *aldehyde* (butyric or valeric aldehyde?). The crude oil revealed the following constants: d_{15} 0.8984; $\alpha_{D} + 11.6$′; $n_{D18°}$ 1.4689; soluble in 1 vol. of 80 p.c. alcohol; E.V. 7.24; cineol content 33· p.c. determined according to phosphoric acid method. Upon rectification 92 p.c. passed over below 183°. The oil contains but few high-boiling constituents, among them a *sesquiterpene*. The presence of phellandrene could not be deter-mined. The oil consists principally of d-*α-pinene* (nitrosochloride) and *cineol*, hence its commercial value is small.

[1]) Report of Schimmel & Co. October 1906, 14. — For older literature on this oil see: Gladstone, Journ. Chem. Soc. 25 (1872), 1 *et seq.*; Pharma-ceutical Journ. III. 2 (1872), 746; Jahresber. d. Chem. 1872, 815. — Maiden, *loc. cit.* 279.

[2]) Journ. and Proceed. Royal Soc. of N.S.W. 41 (1907), 207; Report of Schimmel & Co. November 1908, 28.

674. Oil of Melaleuca pauciflora.

Baker and Smith[1]) distilled the leaves and twigs, collected along the coast of New South Wales, of *Melaleuca pauciflora,* Turcz. and obtained 0.3 p.c. of a viscid oil of a dark amber color. It had the following properties: $d_{15°}$ 0.9302; α_D +3.3°; $n_{D21°}$ 1.4921; S.V. 8.25; scarcely soluble in 10 vol. of 80 p.c. alcohol. It contained 8.7 p.c. of *cineol* (resorcinol method). Another oil had $d_{15°}$ 0.9552; $n_{D24°}$ 1.4923. Pinene was not found. The oil probably contains limonene or dipentene. Possibly the oil contains terpinyl acetate, also about 5 p.c. of free terpineol. Not less than 67 p.c. of the oil distilled over between 260 and 270°. The principal constituent, therefore, appears to be a *sesquiterpene.* Fraction 260 to 270° had the following constants: $d_{15°}$ 0.9364; α_D +8.5°; $n_{D21°}$ 1.5004. It yields characteristic color reactions with glacial acetic acid and sulphuric acid (red color), with acetic acid anhydride and sulphuric acid (green color) and with bromine vapors (blue color). Upon standing the last-mentioned color changes to violet and then to green. It would appear that this sesquiterpene occurs in many of the high boiling portions of many Melaleuca oils.

675. Oil of Melaleuca squarrosa.

The leaves of *Melaleuca squarrosa,* Sm. yield 0.002 p.c. of a green oil with an unpleasant taste[2]).

676. Oil of Melaleuca trichostachya.

The oil of *Melaleuca trichostachya,* Lindl.[3]) has been distilled by Baker and Smith[4]) with a yield of 1.25 to 2.58 p.c. from the dry leaves. It had the following properties: $d_{15°}$ 0.9144 to 0.9153; α_D + 2.3 to + 3.1°; $n_{D20°}$ 1.4636 to 1.4655; S.V. 2.1 to 2.8; E.V. after acetylation 13.9; soluble in 1.3 vol. of 70 p.c.

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[1]) Journ. and Proceed. Royal Soc. of N.S.W. 45 (1911), 312; Report of Schimmel & Co. October 1912, 81.

[2]) Maiden, *loc. cit.* p. 279.

[3]) According to Baker and Smith *Melaleuca trichostachya* and *M. linariifolia* are not synonymous, but true species.

[4]) Journ. and Proceed. Royal Soc. of N.S.W. 44 (1910), 592; Report of Schimmel & Co. April 1912, 93.

alcohol. In addition to almost 80 p.c. *cineol* (resorcinol method)
the oil probably contains pinene. Of esters the presence of
terpinyl acetate was proven. The terpineol was identified by
the reaction with hydrogen iodide (formation of dipentene di-
hydriodide melting at 77°). In addition the oil contains traces
of *phenols,* low-boiling *aldehydes,* also a *sesquiterpene* (?),
d 0.934; n_D 1.4985.

677. Oil of Melaleuca thymifolia.

Melaleuca thymifolia, Sm. is known as thyme-leaved tea tree
in Australia. From leaves distilled in April, Baker and Smith[1])
obtained 2.28 p.c. of volatile oil of a faint yellow color. It had
the properties of good eucalyptus oil, rich in cineol, but was
much more difficultly soluble. $d_{15°}$ 0.9134; $\alpha_{D23°} + 2.1°$; $n_{D23°}$
1.4665; S.V. 3.1; E.V. after acetylation 33.6; insoluble in 10 vol.
of 70 p.c. alcohol, soluble in 0.5 vol. of 80 p.c. alcohol, but the
addition of more alcohol causes turbidity. Its behavior toward
90 p.c. alcohol is similar.

For the most part (86 p.c.) the oil distills between 172 and
183°. The *cineol* assay (phosphoric acid method) yielded 53 p.c.
Very small amounts of *aldehyde* were found present, but neither
pinene nor phellandrene. Judging from the odor, the alcoholic
constituent of the oil seems to be related to borneol.

678. Oil of Melaleuca uncinata.

From leaves and twigs of *Melaleuca uncinata,* R. Br. col-
lected in March, Baker and Smith[2]) obtained 1.246 p.c. of a
yellowish oil. The crude oil of several distillations which lasted
from 4 to 5 hours each, had the following constants: $d_{15°}$ 0.9259;
$\alpha_D + 7.2°$; $n_{D15°}$ 1.4788; S.V. 3.05; soluble in 1.5 vol. of 70 p.c.
alcohol. Upon fractionation only 4 p.c. passed over below 172°,
41.6 p.c. between 172 and 177°, 24.8 p.c. between 177 and 195°,
2.6 p.c. between 195 and 197°, leaving 27 p.c. of higher boiling
constituents. After several days this residue congealed to a

[1]) Journ. and Proceed. Royal Soc. of N.S.W. 40 (1906), 62; Report of
Schimmel & Co. April 1907, 14.
[2]) Journ. and Proceed. Royal Soc. of N.S.W. 41 (1907), 196; Report of
Schimmel & Co. November 1908, 28.

thick mass. The oil contains much *cineol*, some d-*α-pinene* (nitrosochloride), a *sesquiterpene*, also a crystalline substance. This proved to be an alcohol which, after repeated purification, was obtained snow white and melted at 72.5°; $[\alpha]_D$ + 36.99° in alcoholic solution. This substance, named *uncineol* by its discoverers, sublimes in needles and has the formula $C_{10}H_{18}O$.

An oil previously described by Schimmel & Co.[1] ($d_{15°}$ 0.925; α_D + 1°40′) contained cineol as principal constituent.

679. Oil of Melaleuca Wilsonii.

The leaves of *Melaleuca Wilsonii*, F. v. Müll. yield 0.024 p.c. of an oil similar to cajuput oil, with a specific gravity of 0.925[2]).

680. Oil of Bæckea frutescens.

The light yellow oil of *Bæckea frutescens*, L. (family *Myrtaceæ*) consists in part, of a *stearoptene*. $d_{27°}$ 0.883[3]).

681. Oil of Darwinia fascicularis.

Darwinia fascicularis, Rudge (family *Myrtaceæ*) is a shrub 2 to 5 ft. in height which, upon distillation, yields from 0.3 to 0.5 p.c. of a fragrant oil[4]). The crude oil is of a rather dark color and has a specific gravity of 0.915 at 19°. When shaken with dilute alkali it becomes so light in color that its optical rotation could be determined, *viz.*, α_D + 1.2°. The oil was soluble in 2 vol. of 90 p.c. alcohol, but not in 70 p.c. alcohol. Schimmel & Co.[5]) determined the following constants: $d_{15°}$ 0.9232; α_D + 1°10′; $n_{D20°}$ 1.47205; E.V. 179.6 = 62.8 p.c. geranyl acetate; E.V. after acetylation 200.6 = 64.9 p.c. of alcohol $C_{10}H_{18}O$ in the original oil.

The chemical investigation[4]) revealed that the oil contained 57 to 65 p.c. of *geranyl acetate* and about 13 p.c. of a free alcohol which could be esterified readily with acetic acid anhydride, and which, in all probability, is *geraniol*.

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[1]) Report of Schimmel & Co. April 1892, 60.

[2]) Maiden, *loc. cit.* p. 280.

[3]) P. van Romburgh, Verslag Plantentuin Buitenzorg 1892, 57.

[4]) Baker and Smith, Journ. and Proceed. Royal Soc. of N. S. W. 33 (1899), 163.

[5]) Report of Schimmel & Co. October 1900, 19.

The corresponding fraction, after saponification with alcoholic potassa in the cold[1]), yielded a solid compound with calcium chloride, which, when decomposed with water, yielded *geraniol*. This was oxidized to citral which, in turn, was characterized as citryl-β-naphthocinchoninic acid.

As was shown by the analysis of the silver salt, the acid component of the ester consists principally of acetic acid with which are admixed small amounts of a high molecular acid.

682. Oil of Darwinia taxifolia.

Baker and Smith[2]) distilled the oil of *Darwinia taxifolia*, A. Cunn. with a yield of 0.313 p.c. $d_{21°}$ 0.8734; α_D — 6.5°; S.V. 14.5 to 16. Aside from about 4 p.c. of low boiling material, the oil distilled between 165 and 255°. The lightest fraction contained l-*pinene*, which was recognized by its boiling point and by its nitrosochloride melting at 103°. The presence of cineol and phellandrene could not be detected. Judging from its odor, the alcohol present in the oil seems to be linalool. Acetylation yielded results indicating the presence of 7.9 p.c. of an *alcohol* $C_{10}H_{18}O$.

Family: ARALIACEÆ.

683. Oil of Aralia nudicaulis.

Wild sarsaparilla, *Aralia nudicaulis*, L. (family *Araliaceæ*) occurs from Canada to the southern part of the United States of North America. Upon distillation of its rhizome with water vapor, W. C. Alpers[3]) obtained 0.04 to 0.12 p.c. of a light yellow volatile oil which possesses a peculiar odor reminding of young carrots. Distilled under a pressure of 80 mm. the larger part of the oil passes over between 185 and 195°, under atmospheric pressure between 260 and 270°. It consists principally of a sesquiter-pene $C_{15}H_{24}$, *araliene*, b.p. 270°; $d_{18°}$ 0.9107; $d_{20°}$ 0.9086; n_D 1.49936; $[\alpha]_D$ — 7 to — 8° (in benzene solution). No solid derivatives were obtained. In addition, the oil contains an oxygenated constituent,

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[1]) Report of Schimmel & Co. October 1900, 19.

[2]) Baker and Smith, Journ. and Proceed. Royal Soc. of N. S. W. 33 (1899), 163.

[3]) Americ. Journ. Pharm. 71 (1899), 370.

which, judged by its high boiling point, belongs to the class of sesquiterpene alcohols. That portion of the oil which boiled around 300° was colored blue.

Family: UMBELLIFERÆ.

684. Laretia Resin Oil.

The gum resin obtained from *Laretia acaulis*, Gill. et Hook., a Chilian umbelliferous plant, has an odor reminding of galbanum and contains *umbelliferone*, also a *terpene*[1]) boiling at 160°.

685. Oil of Eryngium campestre.

The oil distilled in Southern France from the fresh herb of *Eryngium campestre*, L. (family *Umbelliferæ*) with a yield of 0.088 p.c.[2]) is of a light yellow color and has a pleasant, rather indefinite odor reminding remotely of the oil of musk grains. $d_{15°}$ 0.9043; α_D — 5°42′; $n_{D20°}$ 1.48518; E.V. 10.47; insoluble in 10 vol. of 80 p.c. alcohol, soluble in 1 vol. and more of 90 p.c. alcohol, the diluted solution showing a slight opalescence.

686. Oil of Eryngium fœtidum.

Distilled in Buitenzorg, *Eryngium fœtidum*, L., an umbelliferous plant known as *walang dœri* in Java, yielded 0.03 p.c. of a volatile oil with the following properties: $d_{26°}$ 0.905; $\alpha_D + 0°42′$; A.V. 29.5; S.V. 65; S.V. after acetylation 327. When heated with alcoholic potassa the oil became very dark so that titration became inaccurate. From the aqueous distillate benzene removed upon shaking a *solid acid*, m.p. 165 to 166°; A.V. about 330[3]).

687. Oil of Anthriscus Cerefolium.

From the fresh fruits of *Anthriscus Cerefolium*, Hoffm. (*Chærophyllum sativum*, Lam., family *Umbelliferæ*, Ger. *Garten-*

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[1]) A.Tschirch, *Die Harze und die Harzbehälter.* 2nd ed. Leipzig 1906, I. p. 358.

[2]) Report of Schimmel & Co. October 1905, 73.

[3]) Jaarb. dep. Landb. in Ned.-Indië, Batavia 1911, 46; 1912, 57; Report of Schimmel & Co. October 1913, 49; April 1914, 53.

kerbel), E. Charabot and L. Pillet[1]) obtained, upon distillation 0.0118 p.c. of a light yellow oil with an anise-like odor reminding of esdragon. It consists for the most part of *methyl chavicol*. Treated with alcoholic potassa, the oil yielded anethol, m.p. 20 to 21°, which was identified by its oxidation to anisic aldehyde.

Upon the distillation of the unripe fruits H. Gutzeit[2]) obtained 27 g. of oil from 10 kg. In the aqueous distillate he identified *ethyl* and *methyl alcohol*.

688. Oil of Sweet Cicely.

The root of the umbelliferous plant *Osmorhiza longistylis*, D. C., known in North America as sweet cicely, sweet root and sweet anise, has a decided odor of anise and fennel[3]). This induced L. Eberhart[4]) to distill the root. He obtained 0.63 p.c. of oil that had a specific gravity of 1.0114 at 10°, congealed at 10 to 12° and reliquified at 16°.

Upon fractionation the oil began to boil at 189°, after which the thermometer rose rapidly to 225°. The bulk passed over between 225 and 230°, whereas from 230 to 280° but little came over. Fraction 226 to 227° consisted, as revealed by its properties, of *anethol*, which, upon oxidation yielded anisic acid melting at 184°.

The fraction boiling about 250° yielded a bromide that crystallized in rhombic plates and melted at 139°. The nature of the compound underlying the bromide was not ascertained.

689. Coriander Oil.

Oleum Coriandri. — Corianderöl. — Essence de Coriandre.

Origin and Production. Coriander oil is distilled from the crushed fruit[5]) of *Coriandrum sativum*, L. The exhausted and dried fruits serve as fodder for animals. They contain 11 to 17 p.c. protein and 11 to 20 p.c. fat[6]). For factory production the Moravian, Thuringian, Russian and Hungarian coriander

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[1]) Bull. Soc. chim. III. 21 (1899), 368.

[2]) Liebig's Annalen 177 (1875), 382.

[3]) H. Green, Americ. Journ. Pharm. 54 (1882), 149.

[4]) Pharm. Rundsch. (New York) 5 (1887), 149.

[5]) The umbelliferous fruits are frequently, though not correctly, designated seeds.

[6]) Uhlitzsch, Die landwirtschaftlichen Versuchsstationen 42 (1893), 60.

only come into consideration. The yield varies between 0.8 and 1.0 p.c. Only in case of emergency are fruits from other districts used, for these are much poorer in oil. Of these the French (yield about 0.4 p.c.), Dutch (0.6 p.c.) and Italian (0.5 p.c.) coriander should be mentioned. The large Moroccan fruit yields even less oil, *viz.*, 0.2 to 0.3 p.c., whereas the East Indian yields least, *viz.*, 0.15 to 0.2 p.c.

Properties. Oil of coriander is a colorless or faintly yellowish liquid with a characteristic coriander-like odor and an aromatic, but mild taste. d_{15° 0.870 to 0.885; $\alpha_D + 8$ to $+ 13^\circ$; n_{D20° 1.463 to 1.476; A.V. up to 5; E.V. 3 to 21. With 2 to 3 vol. of 70 p.c. alcohol the oil yields a clear solution at 20°.

Composition. The principal constituent of the oil was recognized by A. Kawalier[1] as a substance of the formula $C_{10}H_{18}O$. Its alcoholic nature was recognized by B. Grosser[2]. F. W. Semmler[3] named it *coriandrol* and recognized that it had an open chain, hence belonged to the so-called olefinic camphors. P. Barbier[4] showed that, with the exception of opposite optical rotation, linalool and coriandrol have the same physical properties and that they are chemically identical. Upon oxidation both yield the same aldehyde, citral, are dehydrated in like manner and can be converted into geraniol by proper chemical treatment. For these reasons coriandrol must be regarded as the dextrogyrate modification of linalool.

The question of the amount of linalool in normal oils has been investigated by H. Walbaum and W. Müller[5]. When acetylated according to the usual manner, the alcohol assay, computed as $C_{10}H_{18}O$, yielded 49.65 p.c.; according to Schimmel & Co's. modification of Boulez's method[6], 67.5 p.c. An attempt to compute the amount of alcohol from the consumed sodium after the dried oil had been heated with this element in toluene solution, yielded 75 p.c. Careful fractionation on a factory scale

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[1] Liebig's Annalen 84 (1852), 351. — Journ. f. prakt. Chem. 58 (1853), 226.
[2] Berl. Berichte 14 (1881), 2485.
[3] *Ibidem* 24 (1891), 206.
[4] Compt. rend. 116 (1893), 1460.
[5] *Wallach-Festschrift*, Göttingen 1909, p. 654.
[6] Report of Schimmel & Co. April 1907, 120.

gave about 70 p.c. d-linalool. Hence the percentage of linalool in coriander oil may be given as between 60 and 70 p.c.

The other constituents have likewise been subjected to a careful investigation by Walbaum and Müller[1]).

In the hydrocarbon fractions, which constitute about 20 p.c. of the oil, the presence of the following compounds has been demonstrated: i-*α-pinene* by means of its nitrolbenzylamide melting at 123 to 124° and *i*-pinonic acid melting at 104 to 105°; d-*α-pinene*[2]) by means of *d*-pinonic acid melting at 68.5 to 70°, $[α]_D + 89.40°$; *β-pinene* by oxidation with permanganate to nopinic acid, m.p. 125 to 127°; furthermore *cymene* with the constants d_{15}, 0.8601, $α_D + 0°$; n_{D20}, 1.48565 was isolated. Upon oxidation with potassium permanganate the cymene yielded *p*-hydroxy *iso*propyl benzoic acid melting at 155 to 156°. *Dipentene* occurs in very small amount only and was identified by means of its tetrabromide melting at 123 to 124°. The presence of both *ter-pinolene* and *phellandrene* was indicated, but the reactions afforded no positive proof. An appreciable proportion of the hydrocarbon fractions consisted of terpinenes, of which *α-terpinene* as well as *γ-terpinene* were identified. With nitrous acid fraction 179 to 180° yielded terpinene nitrosite melting at 154 to 155°. The same fraction yielded with gaseous hydrogen chloride a good yield of terpinene dihydrochloride, m.p. 51 to 52°. The dihydro-bromide melted at 58.5 to 59.5°. The hydrochloride, when treated according to Wallach[3]) with alkali, was converted smoothly into terpinenol. When the terpinene fractions were oxidized with dilute potassium permanganate solution the erythrol melting at 235 to 236° resulted. According to the investigations of Wallach[4]) this is derivable from *γ*-terpinene. In addition the inactive *α, α'*-dihydroxy-*α, α'*-methyl *iso*propyl adipic acid, m.p. 189°, was prepared. This acid is a derivative of *α*-terpinene. Thus it was shown that both terpinenes occur in nature.

In those fractions of coriander oil that boiled higher than linalool, higher members of the fatty aldehydes, principally *decylic aldehyde,* were found, furthermore *geraniol, borneol* and also

[1]) *Wallach-Festschrift*, Göttingen 1909, p. 654.
[2]) Comp. also Report of Schimmel & Co. April 1892, 22.
[3]) Liebig's Annalen 350 (1906), 155.
[4]) *Ibidem* 362 (1908), 296.

the *acetic esters* of these alcohols. The decylic aldehyde was characterized by converting it into decylic acid and into its semicarbazone melting at 102°. In addition to decylic aldehyde other readily changeable aldehydes seem to be present. The geraniol, purified by means of its calcium chloride compound, revealed the constants characteristic of this alcohol: b.p. 231 to 232°; $d_{15°}$ 0.881; $\alpha_D \pm 0°$. It yielded the diphenylurethane melting at 80 to 81°. The isolated borneol was slightly lævogyrate and crystallized from petroleum ether in hexagonal plates melting at 204°. Upon oxidation it yielded camphor, the oxime of which melted at 118°. In the saponification liquid of the esters the presence of acetic acid and some decylic acid was demonstrated.

Hence of the constituents of coriander oil the following are now known: —

d-*α-pinene*, i-*α-pinene*, *β-pinene*, *phellandrene* (?), p-*cymene*, *dipentene*, *α-terpinene*, *γ-terpinene*, *terpinolene* (?), n-*decylic aldehyde*, d-*linalool*, *geraniol*, l-*borneol*, and the *acetic esters* of these alcohols.

Examination. Oil of coriander is frequently adulterated with orange oil or turpentine oil. Their presence is readily indicated by the specific gravity and angle of rotation. Very serviceable for the detection of adulterants is also the solubility in 70 p.c. alcohol. Oils which are not soluble in 3 vol. of this reagent should be rejected.

In order to study the changes which the volatile oil undergoes during the maturing process of the fruits, Schimmel & Co.[1] distilled coriander at various stages. To begin with, fresh, flowering plants, root and all, were subjected to distillation immediately after collection (1). At this stage the plant had an exceedingly disagreeable, benumbing odor of bed bugs. Later when the herb was half-mature and seeds had begun to form a second distillation was carried out (2). The bed bug odor was less prominent and the typical coriander odor became noticeable. Inasmuch as the herb has scarcely any odor when the fruits have reached maturity, the ripe fruits only were used for the third distillation immediately after the harvest (3).

[1] Report of Schimmel & Co October 1895, 21.

1. Oil from the fresh, flowering entire plant.

Yield 0.12 p.c.; $d_{15°}$ 0.853; not soluble in 70 p.c. alcohol; odor exceedingly disagreeable, bed-bug-like. After $2^{1}/_{2}$ months the specific gravity had increased to 0.856. The angle of rotation (not determined in the beginning) was $+$ 1° 2'. The bed-bug-like odor had disappeared completely. Hence the bearers of this odor must have been polymerized or otherwise changed.

2. Oil from the fresh, half-mature herb and fruits.

Yield 0.17 p.c.; $d_{15°}$ 0.866; $\alpha_D +$ 7° 10'; soluble in 3 vol. of 70 p.c. alcohol; odor coriander-like with a trace of the bed-bug odor. After a month the specific gravity had increased to 0.869.

3. Oil from the mature coriander fruit distilled immediately after the harvest.

Yield 0.83 p.c.; $d_{15°}$ 0.876; $\alpha_D +$ 10° 48'; soluble in 3 vol. of 70 p.c. alcohol. Odor pure coriander-like.

690. Oil of Conium maculatum.

OIL FROM THE HERB.

From the herb, without flowers, of *Conium maculatum,* L. (Ger. *gefleckter Wasserschierling,* family *Umbelliferæ*), H. Haensel[1]) obtained 0.0765 to 0.0783 p.c. of a blackish-brown oil from which a stearoptene separated at low temperature. $d_{15°}$ 0.9502; A. V. about 60; S. V. about 70. Upon rectification with water vapor only 25 p.c. of oil passed over; $d_{20°}$ 0.9310; $\alpha_{D20°}$ — 12.4°; S.V. 36. In the blackish-brown residue *palmitic acid* was identified by its melting point and silver salt.

OIL FROM THE FRUITS.

Yield 0.0179 p.c. of a blackish-brown oil[1]); $d_{15°}$ 0.8948; S.V. 34.11. Upon rectification 51 p.c. of oil passed over; $d_{15°}$ 0.8313; α_D — 2.16°.

[1]) Apotheker Ztg. 19 (1904), 557, 558.

691. Oil of Bupleurum fruticosum.

Origin and Production. The oil from *Bupleurum fruticosum*, L., an umbelliferous plant which grows abundantly in Sardinia has been prepared by L. Francesconi and G. Sanna[1]). For distillation plants in various stages of development and from different places were collected. The oil content increased with the development of the plant and the flowers contain more oil than the leaves. Plants growing at higher altitudes are richer in oil than those growing in the plains. Density, optical rotation and index of refraction increase with the growth of the plant, attain a maximum during the flowering period and then decrease. The ester content decreases during the flowering period and is greatest for plants growing in the mountains. Leaf oils contain more ester than flower oils; plants, which have grown in moist places, are poor in esters. Oils rich in ester have a higher specific gravity and a lower angle of rotation than oils poor in ester. The flower oils contain more free alcohol than the leaf oils. During the flowering period the free alcohol content increases at the expense of the esterified alcohol.

From a phytophysiological point of view the investigations of Francesconi and Sernagiotto[2]) on the localization and distribution of the volatile oil in the *Bupleurum* plant are also of interest. The younger the leaves, the more volatile oil they contain. Besides by the method of extraction, the oil can be localized microscopically by means of osmic acid, Soudan III (amidoazo benzolazo-β-naphthol) and Mesnard's reagent.

The branches which had dried somewhat during transportation, and which had been distilled in Laconi (province of Cagliari), yielded 1 p.c. of oil; the leaves during the flowering period 1 to 3 p.c.; and the flowers themselves 3.75 p.c. The entire plant gave a yield of from 0.5 to 4.4 p.c.

Properties. The oils distilled from the several parts of the plant differ as to their properties. The degree of development of the plant, also its locality, influence the properties as will become apparent from the following table: —

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[1]) Gazz. chim. ital. 41 (1911), I. 395; Chem. Zentralbl. 1911, II. 690.
[2]) Atti R. Accad. dei Lincei, Roma (5), 20 (1911), II. 111; Chem. Zentralbl. 1911, II. 1540.

Source of oil:	$d_{15°}$	$[\alpha]_D$	$n_{D22°}$	S. V.	S. V. after acetyl.
a) Botanical Garden of Cagliari (altitude 5 to 10 m.).					
Leaves before flowering . . .	0.8317	$+$ 47.24° (19°)	1.4817	—	—
„ at beginning of flowering period	0.8359	$+$ 45.5° (24°)	1.4841	—	—
„ during height of flowering period	0.8347	$+$ 43.26° (23°)	1.4783	5	—
Branches	—	—	1.4945	—	—
b) Monteponi (altitude 100 m.), Beginning of flowering period.					
Leaves, fresh	0.8576	$+$ 20.48° (24°)	1.4859	14	—
„ dry	0.8594	$+$ 19.72° (24°)	1.4856	13.8	23.7
„ damaged	0.8626	$+$ 19.98° (23°)	1.4862	14	—
c) Buggeru (altitude 60 m.), advanced flowering period.					
Leaves	0.8692	$+$ 41.45° (23°)	—	7	24.8
Branches	0.8484	$+$ 27.06°	—	9	24.3
Flowers	0.8545	$+$ 43.42° (25°)	—	8	28.5
d) Laconi (altitude 500 to 600 m.), at the close of the flowering period.					
Leaves	0.8484	$+$ 28.76° (28°)	—	9.65	—
Branches	0.8441	$+$ 24.49° (28°)	—	8	—
Flowers	0.8517	$+$ 25.26° (28°)	—	8	—
Flowers[1]	0.8593 (13°)	$+$ 32.09°	1.4806 (16°)	8.81	22.9

Composition. Besides an alcohol and an ester, the oil contains a large amount of a terpene[2] which resembles limonene and which has the following properties: b.p. 167 to 169°; d_{14}. 0.8416; $[\alpha]_{D17°}$ $+$ 35.7°; n 1.4862. At 200° it polymerizes to an amorphous, white mass; b.p. 90 to 100°; $[\alpha]_D$ $-$ 66.14°.

If to 5 cc. of oil, dissolved in 20 cc. alcohol, 7 cc. of amyl nitrite or 11 cc. of ethyl nitrite be added, and then 8.5 to 9 cc. of saturated alcoholic (96 p.c.) hydrogen chloride, a nitrosochloride[3] is obtained which probably represents a mixture,

[1] L. Francesconi and E. Sernagiotto, Atti R. Accad. dei Lincei, Roma (5), 22 (1913), I. 34; Chem. Zentralbl. 1913, I. 1114.

[2] L. Francesconi and G. Sanna, Gazz. chim. ital. 41 (1911), I. 796; Chem. Zentralbl. 1911, II. 1450.

[3] L. Francesconi and E. Sernagiotto, Atti R. Accad. dei Lincei, Roma (5), 20 (1911), II. 190; Chem. Zentralbl. 1911, II. 1805.

which melts between 80 and 97°, mostly at 92 to 94°; $[\alpha]_{\mathrm{D}}$ −196.2 to −210.6°. By fractional precipitation of the chloroform solution with methyl alcohol it can be resolved into a less soluble portion that melts at 100 to 101° ($[\alpha]_{\mathrm{D}}$ −285°) and a more readily soluble portion that melts at 101 to 102° ($[\alpha]_{\mathrm{D}}$ −175°). By splitting off nitrosyl chloride from the nitrosochloride, d-*β-phellandrene* ($[\alpha]_{\mathrm{D}}$ +19.65 to +53.32°) was obtained[1]. However, it is doubtful whether the oil contains phellandrene. Upon prolonged boiling of the nitrosochloride with a mixture of 3 parts of water and 10 parts acetic acid there resulted dihydrocuminic aldehyde[2]; b.p. 136 to 140° under 15 mm. pressure; $d_{18°}$ 0.9825; n 1.528; m.p. of semicarbazone 197 to 198°. Oxidized in alcoholic solution with silver oxide the dihydrocuminic aldehyde yielded cuminic acid melting at 116 to 117°.

Upon treating the oil with phthalic acid anhydride Francesconi and Sernagiotto[3] obtained an acid phthalate from which they regenerated an alcohol which they named *bupleurol*. They also isolated an oily compound $C_{10}H_{16}O$ with a pungent odor; d 0.9264; $[\alpha]_D$ +14.93°; n_D 1.4909. Its constitution is unknown.

Bupleurol is an almost colorless oil with a faint rose-like odor; b.p. 209 to 210° (762 mm.); $d_{17°}$ 0.8490; $[\alpha]_{\mathrm{D}}$ +0°; n_{D} 1.4508. Its dibromide is oily. The acid phthalic ester yielded a silver salt that melted at 135°. Bupleurolphenylurethane melts at 45°. Oxidized with Beckmann's mixture, bupleurol yields two aldehydes, the semicarbazones of which melted at 135 and 97° respectively. There also results a yellowish, oily ketone, b.p. 217°, the semicarbazone of which melts at 189 to 190°. Moreover, there was obtained a non-volatile, red oil, b.p. 207° (pressure?), presumably an ester of the original alcohol with the acid resulting upon oxidation. The same oxidation, finally, yielded a free acid, a yellow oil; n_D 1.4370. Francesconi and Sernagiotto regard bupleurol as an aliphatic alcohol differing from citronellol and androl and being characterized by the following formula: —

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[1] Francesconi and Sernagiotto, Atti R. Accad. dei Lincei, Roma (5), 20 (1911), II. 325; Chem. Zentralbl. 1912, I. 345.

[2] Francesconi and Sernagiotto, Atti R. Accad. dei Lincei, Roma (5), 20 (1911), II. 388; Chem. Zentralbl. 1912, I. 345.

[3] Atti R. Accad. dei Lincei, Roma (5), 22 (1913), I. 34; Chem. Zentralbl. 1913, I. 1114.

$$H_3C \diagdown$$
$$CH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C \cdot CH_2 \cdot CH_2 \cdot OH,$$
$$H_3C \diagup \overset{\cdots}{C}H_2$$
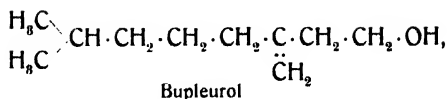
Bupleurol

They regard it as a dihydronerol(?). They fail, however, to supply direct proof for the correctness of the structural formula adopted by them and base their conclusions on purely theoretical considerations[1]). It is assumed that the bupleural, obtained by oxidation of bupleurol, and the above-mentioned ketone are characterized by the following formulas:—

$$CH_2 \cdot CH(CH_3)_2 \qquad\qquad CH \cdot CH(CH_3)_2$$

H_2C $\quad$ CHO	H_2C $\diagup$ $\diagdown$ CO
$H_2C \diagdown$ $\diagup CH_2$	$H_2C \diagdown$ $\diagup$ CH_2
$C:CH_2$	$C:CH_2$

Bupleural. $\qquad\qquad$ Cyclic ketone.
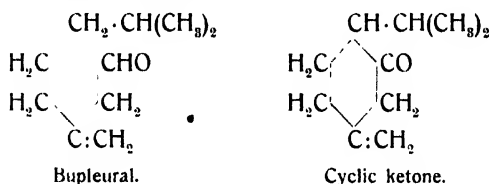
692. Oil of Cumin.

Oleum Cumini. — Cuminöl. — Essence de Cumin.

Origin and Production. Cumin oil is distilled from the fruits of *Cuminum Cyminum,* L., Ger. *römischer Kümmel.* As to the commercial article, the principal countries of production are Morocco, Malta, Syria and the East Indies. Distilled on a technological scale the several kinds gave the following yields:—

Maltese	cumin . . .	3.5 to 4.5 p.c.
Moroccan	„ . . .	3 p.c.
East Indian	„ . . .	3 to 3.5 p.c.
Syrian	„ . . .	2.5 to 4 p.c.

Properties. Fresh cumin oil is colorless, but later becomes yellow and even brown. It has the unpleasant bed-bug-like but characteristic cumin odor and a spicy, somewhat bitter taste.

$d_{15°}$ 0.900 to 0.930 (in connection with an East Indian oil and two oils of unknown origin the density was found from 0.893 to 0.899); $\alpha_D + 3° 20'$ to $+ 8°$; $n_{D20°}$ 1.494 to 1.507; soluble in 3 to 10 vol. and more of 80 p.c. alcohol, the denser oils

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[1]) Atti R. Accad. dei Lincei, Roma (5), **22** (1913), I. 148; Chem. Zentralbl. 1913, I. 1508.

being the more readily soluble ones. Attempts to assay the cuminic aldehyde failed to give satisfactory results either with sodium acid sulphite or with neutral sulphite. The acid sulphite method yielded results varying between 23 and 30 p.c. for the same oil, moreover the strong odor of the residual oil revealed the presence of considerable amounts of cuminic aldehyde after the assay. The phenylhydrazine method, which yielded accurate results[1]) to within 1 to 2 p.c. error revealed 35 to 42 p.c.

Composition. The constituent to which oil of cumin owes its odor and its principal properties is the *cuminic aldehyde* or *cuminol*[2]) the properties and derivatives of which have been described in Vol. I, p. 422. This aldehyde is accompanied by *cymene* and *terpenes*.

In order to separate the hydrocarbons from the oxygenated constituents, C. Gerhardt and A. Cahours[3]) distilled the oil with caustic potassa, whereby the aldehyde was converted into cuminic acid on the one hand and cuminic alcohol in the other, thus holding them back. C. Bertagnini[4]) found that it combines with sodium acid sulphite and thus recognized the aldehyde nature of cuminol. Thus the way was paved for the isolation of this substance. According to C. Kraut[5]) the low-boiling portions are first distilled off and the residue shaken with sodium acid sulphite. After standing for twenty-four hours the magma is expressed and decomposed by distillation with soda solution or dilute sulphuric acid.

The occurrence of a terpene in cumin oil was first ascertained by C. M. Warren[6]) and later verified by F. Beilstein and A. Kupfer[7]). Inasmuch as L. J. Wolfram[8]) was unable to prepare a crystalline derivative and thus to identify the hydrocarbon with one of the known terpenes, he assumed that he had found a

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[1]) Report of Schimmel & Co. April 1913, 45.

[2]) Cumina*l* would be the proper designation in order to point out its aldehyde character.

[3]) Liebig's Annalen 38 (1841), 70.

[4]) *Ibidem* 85 (1853), 275.

[5]) *Ibidem* 92 (1854), 66.

[6]) Jahrb. d. Chem. 1865, 514; See also R. Fittig, Zeitschr. f. Chemie 1, N. F. (1865), 667; Pharm. Zentralbl. 1866, 150.

[7]) Liebig's Annalen 170 (1873), 282.

[8]) Pharm. Zeitschr. f. Russl. 35 (1896), 97, 113, 129, 145, 161.

new terpene which gave liquid derivatives only and called it
hydrocuminene.

The second hydrocarbon of cumin oil is cymene, the identity
of which with the cymene from camphor and from other volatile
oils was demonstrated by Beilstein and Kupfer, also by Wolfram.

A more recent investigation conducted in the laboratory of
Schimmel & Co.[1]) has revealed that the terpene fraction of the
oil consists of several hydrocarbons. ·

Fractionation in vacuum of an oil distilled by themselves
effected the separation of the hydrocarbons from the higher-
boiling constituents. The fractions boiling above 80° (10 mm)
were shaken with acid sulphite and the hydrocarbons, the aldehyde
and non-aldehydic higher-boiling portions examined separately.

The hydrocarbons separated by vacuum distillation were
fractionated repeatedly under diminished pressure. With in-
creasing boiling point the optical rotation decreased appreciably.
Thus, whereas fraction 168 to 169° had an $\alpha_D + 14°40'$, fraction
178° showed an $\alpha_D + 0°35'$ only. After repeated fractionation
of $2^1/_2$ kg. of hydrocarbons, 11 g. of a fraction 158 to 168° were
obtained which had an odor of pinene. With nitrosylchloride
a very small yield of nitrosochloride was obtained, the benzyl-
amine derivative of which melted at 120 to 123°. The presence
of d-*α-pinene* was proven by the oxidation to active *d*-pinonic
acid, m. p. 68 to 69°. Hence the oil contains both *i*- and
d-α-pinene, though in minimal amounts only.

In addition to *p*-cymene (m. p. of hydroxy*iso*propyl benzoic
acid 155 to 156°), the higher-boiling hydrocarbon fractions contain
small amounts of terpenes. Upon oxidation of the cymene
fraction a small amount of sodium nopinate was obtained. The
free nopinic acid, m. p. 125 to 126°, was lævogyrate. Further
oxidation with permanganate yielded nopinone (m. p. of semi-
carbazone 187 to 188°), thus proving the presence of *β-pinene*.

Fraction 178° ($\alpha_D + 0°35'$) added about 10 p.c. of bromine.
With hydrogen chloride a solid dihydrochloride, m.p. 48°, resulted,
which when mixed with dipentene dihydrochloride suffered no
melting point depression. From the same fraction a nitroso-
chloride was obtained. It was obtained in small amount and

[1]) Report of Schimmel & Co. October 1909, 49.

crystallized only after the addition of water, alcohol and ether. These facts indicate *dipentene.*

Although the presence of phellandrene could not be proven directly, for the nitrite reaction gave negative results, the presence of *β-phellandrene* is rendered probable by the results of the oxidation experiments. From the oxidation mother-liquids with 1 p.c. permanganate solution, a glycol was isolated as a viscid oil that would not congeal. Treated with dilute sulphuric acid, a substance with a decided cumin odor resulted, the semicarbazone of which melted at 205 to 208 . The aldehyde regenerated therefrom yielded, upon oxidation, cuminic acid melting at 113 to 115°. Hence this fraction must contain a hydrocarbon with a methene group directly in touch with the nucleus, for only such a combination is capable of yielding a glycol which, upon dehydration, may yield an aldehyde of the cumin series. In addition to the glycol a number of oily acids had resulted. *Iso*butyric acid was the only one isolated (b. p. 157 to 159°); the calcium salt was more difficultly soluble in hot than in cold water. It was impossible to ascertain with certainty from which hydrocarbon these oxidation products were derived. It may not be farfetched, however, to assume that they owe their formation to *β*-phellandrene, for the presence of *β*-terpinene, which might yield similar products, could not be ascertained by other methods.

The acid sulphite compound, having been purified with alcohol and ether, was decomposed with soda solution, and the aldehyde distilled with water vapor and its constants determined: b. p. 97 to 99° (7 mm.); $d_{15°}$ 0.9731; $a_D + 0°3'$. Oxidized with chromic acid, the aldehyde yielded cuminic acid melting at 113 to 114°. Its semicarbazone melted at 210 to 211°, its oxime at 55 to 57°[1]).

It was remarkable that the first fraction of the aldehyde should be slightly dextrogyrate ($a_D + 1°13'$). Upon oxidation, however, cuminic acid only resulted. Upon fractional crystallization of the semicarbazone there was obtained, in addition to laminar crystals of the cuminic aldehyde semicarbazone melting at 210 to 211°, another crystallizing in fine prisms that melted at 200 to 201° (perilla aldehyde?). Upon oxidation of the underlying aldehyde

[1]) Wallach (Liebig's Annalen 840 [1905], 6) gives the melting point as 58 to 59° whereas Westenberger (Berl. Berichte 16 [1883], 2994) found it at 52°.

cuminic acid also was obtained. The oxime melted between 72 and 76° (impure). Hence it may be assumed that, in addition to cuminic aldehyde, a *hydrocuminic aldehyde* is likewise present.

The higher boiling portions of the oil that did not react with acid sulphite nevertheless had the typical odor of cuminol, hence still contained traces of aldehyde which were removed by repeated shaking with semicarbazide solution. From 12 kg. of cumin oil there were obtained about 20 g. that boiled between 100 and 115° (7 mm.), and the E.V. of which, after acetylation, was 211. Attempts to prepare characteristic derivatives were unsuccessful. Oxidation with permanganate, however, yielded cuminic acid melting at 112 to 113°. Inasmuch as the cuminic aldehyde had been carefully removed from the oil, this constituent must be *cuminic alcohol*. In addition to this alcohol there is present a small amount of a substance boiling between 90 and 107° (3 mm.).

693. Oil of Celery Fruits.

Oleum Apii graveolentis seminis. - Selleriesamenöl. — Essences de Semence de Céleri.

Origin and Production. Volatile oil is contained in all parts of the celery plant, *Apium graveolens,* L., but most abundantly in the fruits. It is present in much smaller amount in the fresh herb though an oil can still be obtained from it. The roots and bulbs contain only traces.

The fruits yield upon distillation with water 2.5 to 3 p.c. of a very limpid, colorless oil that has a strong odor and taste of celery.

Properties. $d_{15°}$ 0.866 to 0.894, mostly above 0.872; $\alpha_D + 60$ to $+82°$; $n_{D20°}$ 1.478 to 1.486; A.V. up to 4; E.V. 16 to 45; E.V. after acetylation[1]) (2 determinations) 43 to 52; soluble in 6 to 8 vol. of 90 p.c. alcohol, mostly with turbidity. Of 95 p.c. alcohol 1 to 1.2 vol. are necessary, but occasionally even with this solvent the solution is opalescent.

Composition. To the extent of at least 70 p.c. celery oil consists of hydrocarbons. An examination in the laboratory of Schimmel & Co.[2]) yielded a fraction that reached a constant boiling

[1]) According to J. Swenholt (Midland Drugg. and Pharm. Review **44** [1910], 220) the acetylation number of the saponified oil is much lower than that of the original oil, a circumstance that is explained by the presence of sedanolid.

[2]) Report of Schimmel & Co. April 1892, 15; April 1910, 32.

point of 176 to 177°, $\alpha_D + 107°$. Bromine yielded a solid bromide melting at 105°. Hence d-*limonene* is a constituent of celery oil. Other terpenes do not appear to be present. Pinene certainly is excluded since nothing passed over below 170°. This is important for it enables the detection of adulteration with turpentine oil.

The amount of oxygenated constituents which provide the typical celery odor is much smaller than the amount of terpenes. Sometimes a separation takes place during the process of distillation, the heavier portions settling to the bottom in the receiving flask. Frequently, however, no heavy oil at all is obtained. This passes over but difficultly with water vapor, hence upon rectification of the oil remains behind in the still.

It was such a residue, also the so-called heavy oils, which was used by G. Ciamician and P. Silber[1]) in an investigation that revealed the following substances: —

1) *Palmitic acid;* 2) a *phenol* with the properties of *guaiacol;* 3) a second *phenol* consisting of white needles melting at 66 to 67° and having the composition $C_{16}H_{20}O_3$; 4) a *sesquiterpene* (see below); 5) *sedanolid,* a lactone $C_{12}H_{18}O_2$, b. p. 185° (17 mm.). The corresponding hydroxy acid, sedanolic acid $C_{12}H_{20}O_3$, melts at 88 to 89° and readily yields sedanolid. Oxidation revealed that sedanolic acid is an o-hydroxyamyl-Δ^6-tetrahydrobenzoic acid; 6) *Sedanonic acid anhydride,* $C_{12}H_{16}O_2$. Sedanonic acid $C_{12}H_{18}O_3$ is an unsaturated ketoacid (m. p. 113°), namely o-valeryl-Δ^1-tetrahydrobenzoic acid. Sedanolid and the anhydride of sedanonic acid are to be regarded as the constituents of celery oil which supply the characteristic odor. Their probable constitution is expressed by the following formulas: —

Sedanolid.   Sedanonic acid anhydride.
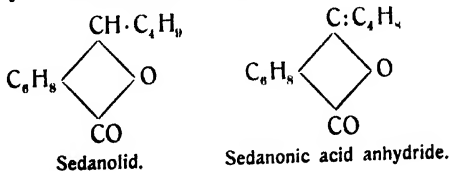
As was shown by an investigation made by Schimmel & Co.[2]), the sesquiterpene referred to above is not identical with any of

¹) Berl. Berichte 80 (1897), 492, 501, 1419, 1424, 1427.
²) Report of Schimmel Co. April 1910, 33.

the known ones. *Selinene,* as the hydrocarbon has been named (from τὸ σέλινον, celery, Ger. *Sellerie*) can readily be identified by means of its hydrochloride. In order to remove any phenols present, the respective fractions were shaken several times with 5 p.c. caustic soda solution, and the separated hydrocarbon distilled over sodium. It distilled between 265 and 273°. The following constants were determined for this product: —

I. Fraction: b.p. 120 to 121° (6 mm.); $d_{17.5°}$ 0.9197; $\alpha_D + 35°11'$; $n_{D21°}$ 1.49863.

II. Fraction: b.p. 121 to 122° (6 mm.); $d_{18°}$ 0.9170; $\alpha_D + 38°12'$; $n_{D21°}$ 1.4956.

By passing hydrogen chloride into the ethereal solution of the hydrocarbon a good yield of solid chloride was obtained which crystallized in needles from the reddish-blue residue after evaporation of the ether. The addition of a small amount of alcohol and refrigeration in a freezing mixture greatly facilitated the crystallization of the chloride. Recrystallized once it melted at 68 to 70°. Repeated recrystallization from methyl alcohol brought the melting point to 72 to 74°.

The composition of the chloride agrees with the formula $C_{15}H_{24}2HCl$. It is optically active in the same direction as is the underlying hydrocarbon. The product recrystallized but once, m.p. 68 to 70°, in a 10.79 p.c. ethereal solution showed a specific rotation $[\alpha]_D + 7°32'$. The product that had been purified repeatedly, in a 4.07 p.c. chloroform solution showed a higher specific rotation of $[\alpha]_D + 18°$.

Upon removal of hydrogen chloride with sodium ethylate a hydrocarbon with the following properties was obtained: b.p. 268 to 272° (the bulk at 268°); $d_{15°}$ 0.9232; $d_{20°}$ 0.9196; $\alpha_D + 49°30'$; $n_{D20°}$ 1.50483, mol. refr. found 65.82, computed for $C_{15}H_{24}/_2$ 66.15. With hydrogen chloride the hydrocarbon, in ethereal solution, is again converted into the dihydrochloride, melting at 72 to 74°.

Further investigation by F. W. Semmler and F. Risse[1]) has revealed that the natural selinene is a mixture, consisting principally of semicyclic pseudo-(β-)selinene and but little ortho-(α-)selinene.

The same investigators have shown that it is advisable to pass a mixture of one part of hydrogen chloride and three parts

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[1]) Berl. Berichte **45** (1912), 3301, 3725; **46** (1913), 599.

of air into the ethereal solution of the sesquiterpene when preparing selinene dihydrochloride. This modification results in a better yield than when undiluted hydrogen chloride gas is used. They regenerated the selinene from its dihydrochloride, not with the aid of sodium ethylate, but with a saturated methyl alcoholic solution of potassium hydroxide. Such a mixture was first set aside at room temperature for several hours, the temperature increased gradually, and finally heated on a water-bath. In this manner they obtained a sesquiterpene with the following properties: b.p. 128 to 132° (11mm.); $d_{20°}$ 0.9190; $\alpha_D +$ 61°36'; n_D 1.50920. These figures agree well with the constants determined by Schimmel & Co., however, the angle of rotation is higher.

As a result of their investigations, which cannot here be given in greater detail, Semmler and Risse proposed the accompanying formula for the semicyclic pseudo-β-selinene.

As to the relative amounts of the individual substances present in the oil, Schimmel & Co. have found that celery oil consists of at least 70 p.c. of hydrocarbons, 60 p.c. being d-*limonene* and about 10 p.c. d-*selinene*. Alcohols that have not been further examined are present to the extent of 2.5 to 3 p.c.

From the high boiling portions 2.5 to 3 p.c. of pure *sedanolid* and 0.5 p.c. of *sedanonic acid anhydride* were isolated. 10 p.c. of the oil remain in the residue upon fractional distillation of the oil.

According to J. Swenholt[1] the aqueous distillate contains acids the analytical value of which would seem to indicate sedanolic and sedanonic acid.
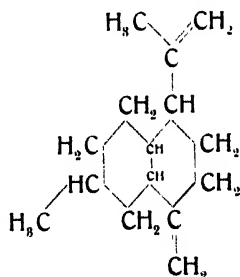
694. Oil of Celery Leaves.

Oleum Apii graveolentis foliorum. — Selleriekrautöl. — Essence de Feuilles de Céleri.

The oil distilled from the fresh herb[2] (yield about 0.1 p.c.), possesses the strong odor of fresh celery leaves to the fullest

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[1] Midland Drugg. and Pharm. Review 44 (1910), 220.
[2] Report of Schimmel & Co. October 1895, 62.

extent. It is limpid and of greenish-yellow color; $d_{15°}$ 0.848 to to 0.880, the density being high when herb with fruits has been employed; $\alpha_D + 41$ to $+ 60°$; $n_{D20°}$ 1.478 to 1.481; A. V. up to 3; E. V. 28 to 52; E. V. after acetylation 33 to 58. The solubility varies, some oils are soluble in 3 to 5 vol. of 90 p.c. alcohol, others require from 7 to 10 volumes. Occasionally a slight turbidity is noticeable. The oils are readily soluble in 0.5 vol. and more of 95 p.c. alcohol.

An oil distilled in southern France from the herb and fruits of the wild celery *(ache des marais)*, was light yellow in color and possessed a strong celery odor. It had the following constants[1]): $d_{15°}$ 0.8713; $\alpha_D + 58°$ 30'; $n_{D20°}$ 1.47715; A. V. 1.8; E. V. 41.5; even with 95 p.c. alcohol a clear solution could not be obtained, the explanation for which was found in the strong resinification of the oil. Rectification with water vapor yielded a residue of 7.7 p.c. and an oil with the following greatly modified properties: $d_{15°}$ 0.8541; $\alpha_D + 70°$ 55'; $n_{D20°}$ 1.47489; soluble with slight turbidity in 6 and more volumes of 90 p.c. alcohol.

An oil distilled in Algeria[2]) from entire wild plants revealed the following properties: $d_{15°}$ 0.8467; $\alpha_D + 69°$ 18'; A. V. 0; S. V. 16.7; E. V. after acetylation 20.9; with 15 vol. of 85 p.c. alcohol it yields a turbid solution, with 4.5 vol. of 90 p.c. alcohol a faint opalescence, and a clear solution in all proportions with 95 p.c. alcohol.

695. Oil of Celery Root.

H. Haensel[3]) has distilled the peeled roots as well as the peelings with the attached rootlets. The oil from the roots proper showed $\alpha_D + 36.5°$, that of the peelings and rootlets $+ 20°$. The total yield computed for the carefully washed and cleaned roots amounted to only 0.009 p.c.

An oil distilled by Schimmel & Co. from herb and roots had the following properties: $d_{15°}$ 0.8816; $\alpha_D + 23°$ 40'; $n_{D20°}$ 1.48393; A. V. 0.8; E. V. 47.7; soluble in 3.5 vol. and more of 90 p.c. alcohol.

[1]) Report of Schimmel & Co. October 1909, 37.

[2]) Berichte von Roure-Bertrand Fils April 1912, 30.

[3]) Apotheker Ztg. 16 (1901), 60.

696. Oil of Parsley.

Oleum Petroselini. — Petersilienöl. - Essence de Persil.

Origin. Parsley, *Petroselinum sativum*, Hoffm. (*Apium Petroselinum*, L., *Carum Petroselinum*, Benth. et Hook.), Ger. *Petersilie,* was originally indigenous to the Mediterranean countries and to central Asia, but it is now cultivated in almost all temperate climates.

Production. Volatile oil is contained in all parts of the plant but is particularly rich in the fruits. Upon distillation these yield 2 to 7 p.c. of oil which enters commerce as parsley oil or parsly seed oil.

Properties. It is a colorless or yellowish or yellowish-green, viscid liquid, the odor of which, though it reminds of the herb, is quite distinct. $d_{15°}$ 1.043 to 1.101; α_D - 4° 30' to — 9° 24'; $n_{D20°}$ 1.512 to 1.523; A. V. up to 6; E. V. 1 to 8; E. V. after acetylation 4 to 20; soluble in 4 to 8 vol. and more of 80 p.c. alcohol, exceptionally with turbidity.

The oil from the German fruits is frequently, though not always, so rich in apiol, that it congeals to a semi-solid mass at ordinary temperature. French fruits, on the other hand, yield an oil much poorer in apiol. Small, poorly developed fruits, as a rule, yield an oil with lower specific gravity and higher angle of rotation.

Composition. The principal constituent of the oil from the fruit is *apiol,* a phenol ether which, in more recent years, has been investigated by E. v. Gerichten[1]), J. Ginsberg[2]), and G. Ciamician and P. Silber[3]). Its constitution was revealed by the two last-mentioned authors and by H. Thoms[4]). Properties and structural formula are recorded in vol. I, p. 490.

According to v. Gerichten, fraction 160 to 164° of parsley oil[5]) has a specific gravity of 0.865 at 12° and in a 100 mm. tube deviates the angle of polarization — 30.8°. When hydrogen chloride was passed into it no solid hydrochloride was obtained

[1]) Berl. Berichte 9 (1876), 258, 1477.
[2]) *Ibidem* 21 (1888), 1192, 2514; 23 (1890), 323.
[3]) *Ibidem* 21 (1888), 913, 1621; 22 (1889), 2481; 23 (1890), 2283.
[4]) *Ibidem* 36 (1903), 1714.
[5]) F. Grünling (Dissertation, Strassburg 1879) found the boiling point of the terpene at 158°.

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directly, but it resulted upon dilution with alcohol and spreading out in a thin layer. In this manner a small amount melting at 115 to 116° resulted. That the underlying hydrocarbon is *α-pinene* was demonstrated by H. Thoms[1]), who obtained a nitrosochloride, m.p. 105°, from the lowest fraction (b.p. 156 to 160°) of a French parsley oil.

Two additional phenol ethers have been found thus far in the French oil, which by no means proves that they are also contained in German parsley oil.

A further investigation of the French oil, in which Thoms[2]) found pinene, yielded traces of *palmitic acid* (m.p. 62°) and of phenols, aldehydes and ketones not farther characterized. A large portion of the oil consisted of *myristicin* (see vol. I, p. 489) which proved to be identical with that of nutmeg oil. Of derivatives dibromomyristicin dibromide (m.p. 130°) and *iso*myristicin (m.p. 44 to 45°) were prepared. C. Bignami and G. Testoni[3]) had previously obtained myristicinic acid upon oxidation of the same fraction of parsley oil and had inferred the presence of a compound with the formula now assigned to myristicin.

Somewhat later Thoms[4]) succeeded in isolating a second phenol ether, the oxidation product of which, tetramethoxy-benzene-1-carboxylic acid, had likewise been obtained by Bignami and Testoni from the oil. Upon submitting the proper fraction to the temperature of solid carbon dioxide, 1-*allyl*-2,3,4,5-*tetra-methoxybenzene,* previously not observed in volatile oils, was separated (see vol. I, p. 492).

According to H. Matthes and W. Heintz[5]), the fatty oil of parsley seeds contain small amounts of a hydrocarbon melting at 69° and named *petrosilane.* Inasmuch as such hydrocarbons are volatile with water vapor the presence of petrosilane in parsley oil is probable.

In order to ascertain what caused the difference in the apiol content of German and French parsley oil, Thoms[4]) under-

[1]) Berl. Berichte **36** (1903), 3453.

[2]) *Ibidem* 3452.

[3]) Gazz. chim. ital. **30** (1900), I. 240; Chem. Zentralbl. **1900**, I. 975.

[4]) Berl. Berichte **41** (1908), 2753.

[5]) Berichte d. deutsch. pharm. Ges. **19** (1909), 325.

took to investigate by means of cultural experiments whether external conditions, such as methods of culture, climate, &c. exercised any influence. The results of these experiments are of interest in several directions. Of French seeds part was distilled directly (Oil I), another portion was sown in Dahlem during the spring of 1904. The fruit harvested in the fall of 1905 was distilled in February 1906 (Oil II). As shown by the data tabulated below, the difference in the composition of the two oils are but slight. It should be mentioned, however, that appreciable differences might be expected only after a succession of cultural periods.

	Oil I	Oil II
$d_{15°}$	1.03	1.07
Terpene content	abt. 5 p.c.	abt. 5 p.c.
Acid mixture (principally palmitic acid)	0.1746 p.c.	0.876 p.c.
Phenols	0.184 p.c.	2.51 p.c.
Principal fractions under 15 mm. pressure		
a) 160 to 165°.	28 p.c.	25 p.c.
b) 165 to 170°.	47 p.c.	35 p.c.

697. Oil of Parsley Root.

The root of parsley contains but very little oil. According to Schimmel & Co.[1]) the yield from the distillation of dry roots amounted to 0.08 p.c., that of fresh roots 0.05 p.c.

$d_{15°}$ 1.049 to 1.1012; α_{D} +1°24′. Even at ordinary temperature the oil separates crystals, presumably of apiol.

698. Oil of Parsley Herb.

The oil of the herb[2]) (yield from the fresh herb 0.016 to 0.3 p.c.) is limpid and of greenish-yellow color. It has the odor of fresh parsley, which is noticeable in the oil of the fruit only to a slight degree. The properties of the oil vary with cultural varieties, the character of the herb (flowering, non-flowering, with fruit, first, second or third cutting); $d_{15°}$ 0.9023 to 1.0157; α_{D} +1°16′ to +4°10′; $n_{D20°}$ 1.509 to 1.525; A.V. up to 1.0; E.V. 5 to 14; E.V. after acetylation 19 to 68. In 95 p.c. alcohol it is soluble

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[1]) Report of Schimmel & Co. April 1894, 55.
[2]) Comp. Report of Schimmel & Co. October 1895, 62.

in wellnigh all proportions. In 90 p.c. alcohol the oils do not
always dissolve to a clear solution, some oils, however, yield an
opalescent to turbid solution with even 2 to 4 volumes. Two oils
of the herb with flowers and fruits just formed had the following
properties: d_{15} 0.9578 and 0.9252; $α_{D}$ — 2° 47′ and — 0° 46′.

699. Oil of Cicuta virosa.

The fruits as well as the roots of the very poisonous *Cicuta
virosa*, L., water hemlock, Ger. *Wasserschierling,* contain volatile oil.

OIL OF THE FRUITS.

Upon distillation of the dried fruits, collected in fall, J. Trapp[1])
obtained 1.2 p.c. of an almost colorless, limpid oil, which was
lighter than water and had the odor and taste of oil of cumin
from *Cuminum Cyminum,* L.

· Shaken with sodium acid sulphite solution it yielded a solid
compound that had the composition of *cuminal* hydroxysulphonate
of sodium. The portion of oil not attacked by the bisulphite solution
yielded a fraction 176° that consisted of *cymene,* yielding cymene
sulphonic acid when treated with fuming sulphuric acid.

Hence the oil of *Cicuta virosa* contains the same con-
stituents found in the oil of *Cuminum Cyminum, viz.,* cuminic
aldehyde and cymene.

OIL FROM THE ROOTS.

Upon distillation the roots yielded 0.12[2]) to 0.36[3]) p.c. of
an oil the odor of which reminded of water fennel and celery,
and the specific gravity of which was 0.870 at 18°. It differs
completely from the oil obtained from the fruits, containing
neither cymene, nor cuminic aldehyde. By means of fractionation
a dextrogyrate terpene, boiling at 166°, "cicutene" was isolated.
When hydrogen chloride was passed into cicutene a hydro-
chloride was obtained which did not congeal to a solid mass
until it was placed in a freezing mixture. In all probability
cicutene is not a chemical individual but consists of a mixture
of several terpenes (pinene and phellandrene?).

[1]) Journ. f. prakt. Chem. 74 (1858), 428.—Arch. der Pharm. 231 (1893), 212.
[2]) E. Simon, Liebig's Annalen 31 (1839), 258.
[3]) A. H. van Ankum, Journ. f. prakt. Chem. 105 (1868), 151.

The oil from the root was formerly regarded as poisonous. That this is not the case was demonstrated by E. Simon[1]) with experiments upon animals.

700. Oil of Cicuta maculata.

Upon distillation the fruits of *Cicuta maculata*, L., a poisonous plant widely distributed on the North American continent, yield 3.8 to 4.8 p.c. of a volatile oil[2]) that has the odor of *Chenopodium anthelminticum* and a specific gravity of 0.840 to 0.855. The principal portion of the oil boils between 176 and 183° and consists of terpenes as was revealed by the analysis of fractions 176 to 178.5° and 178 to 183°.

701. Oil of Caraway.
Oleum Carvi. - Kümmelöl. - Essence de Carvi.

Origin and Production. Caraway, *Carum Carvi*, L., Ger. *Kümmel*, which occurs wild in northern and central Europa and in several of the South European countries, also in various parts of Asia, is cultivated, more particularly in Holland, for its aromatic fruits. The caraway fruit, the „Kümmel" of commerce is used either as such as spice or in the preparation of "Kümmel", the liqueur, or distilled for its volatile oil.

In order to exhaust the caraway completely of its oil, the fruits are crushed between revolving rollers. When crushed, the fruits should be distilled at once, otherwise they will suffer considerable loss of oil. At the beginning of the distillation an appreciable development of hydrogen sulphide becomes noticeable, as to the causes of which there is some doubt. This phenomenon, observable also in connection with other umbelliferous fruits, was noticed as early as 1823 by Planche[3]).

Modern stills (fig. 50, vol. I. p. 238) have a capacity of about 2500 kg. caraway which is made to yield its oil completely in 6 to 8 hours. Formerly it was rather common to distill the fruit in its entire condition, a practice that still seems

[1]) Liebig's Annalen 31 (1839), 258. See also L. H. Pammel, Pharm. Rundsch. (New York) 13 (1895), 103.

[2]) R. Glenk, Americ. Journ. Pharm. 63 (1891), 330.—F. P. Stroup, *ibidem* 68 (1896), 236.

[3]) Trommsdorff's Neues Journ. der Pharm. 7 (1823), I. 358.

to obtain, in part, today. In this manner the fruits are not exhausted completely, hence the yield is smaller, a difference, however, which is more than equalized by the sale of the dried fruits. These are used in the production of cheese and as adulterant. — Distilled caraway differs from the fresh by its darker color, the wellnigh absence complete of odor and taste, and by the shrivelled appearance of the fruit. Under the microscope the cross section reveals the empty oil reservoirs and the ruptured cells of the outer layer.

The exhausted, crushed caraway is dried in special apparatus[1] and is used as nutritious and highly valued fodder for animals. According to a series of analyses made in the Agricultural Experiment Station in Möckern, near Leipzig[2]), the dried caraway fodder contains 20 to 23.5 p.c. crude protein, 75 to 85 p.c. of which is digestible, and 14 to 16 p.c. fat.

The oil yield varies according to the geographic source of the fruit. For the various commercial varieties of caraway Schimmel & Co. ascertained the following average values:—

Bavarian, wild . . . 6.5 to 7 p.c.	Norwegian, wild . . . 5 to 6.5 p.c.
German, cultivated . . 3.1 „ 5 „	East Frisian . . . . 5.5 „ 6 „
Bohemian . . . . . 5.3 „	East Prussian, cultivated 5 „ 6.2 „
Finnish, wild . . . . 5 „ 6 „	Russian, wild . . . . 3.2 „ 3.6 „
Galician . . . . . 4.5 „	Swedish, wild . . . . 4 „ 6.5 „
Hessian, wild . . . 6 „ 7 „	Styrian . . . . . . 6 „
Dutch, cultivated . . 4 „ 6.5 „	Tirolese, wild . . . . 6.5 „
Moravian . . . . . 4 „	Württemberg, wild . . 5.5 „ 6 „

For the purpose of distillation the Dutch, Norwegian, and East Prussian caraway come into consideration. The caraway cultivated in other places of northern Germany is not suitable for oil distillation, in spite of its good appearance, because the oil content is low.

As to the profitability, yield is not the only factor, but the quality of the oil as well which is judged by its carvone content. This, in turn, is indicated by the specific gravity. It may happen

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[1]) Muspratt-Stohmann, *Technische Chemie.* IV. ed. Leipzig 1888. vol. I. p. 67. .

[2]) Uhlitzsch, Die landwirtschaftl. Versuchsstationen 42 (1893), 48; comp. also F. Honcamp, Sächsische landwirtschaftl. Zeitschr. 1907, 953.

Fig. 23. Dutch caraway field (to the right) in its first year.

Fig. 24. Mowing of caraway in Holland.

that the distillation of a caraway with a low yield of oil with higher density pays better than that of a fruit with large oil yield but lower density.

For the preparation of carvone (carvol, *Oleum Carvi* of the Ph. G. IV.) caraway oil is fractionated either in vacuum or with steam. When the density has reached 0.960 the fraction is collected separately as carvone. The by-product containing limonene, the "carvene", has a specific gravity of 0.850 and finds use as a cheap soap perfume.

Production and Commerce. Detailed figures are available only for Holland, the principal producing country. As for the other producing districts, East Prussia, Scandinavia and Finland, scarcely any statistical material has been published[1]).

According to the official Dutch reports, most of which have been republished in the Report of Schimmel & Co., the areas cultivated in the several provinces, the average yield per hectare, and the total crop are as follows:—

	1905 Hectares	1905 Bales pro ha	1905 Bales total	1906 Hectares	1906 Bales pro ha	1906 Bales total	1907 Hectares	1907 Bales pro ha.	1907 Bales total
North Holland	2019	23.7	47884	1961	20.7	40509	2200	22.7	49957
Seeland . . .	825	22.6	18648	763	21.8	16632	703	25.4	17834
North Brabant	770	19.5	15001	732	21.3	15622	655	20.6	13504
Groningen . .	434	22.1	10914	947	24.1	22698	1162	25.7	29892
Friesland. . .	26	23.3	606	49	19.5	955	33	23.0	760
South Holland	209	23.8	4964	175	23.9	4184	163	23.9	3901
Utrecht . . .	12	30.0	360	9	25.0	225	9	20.0	180
Total:	4295	22.9	98377	4636	21.8	100825	4925	23.6	116028

	1908 Hectares	1908 Bales pro ha	1908 Bales total	1909 Hectares	1909 Bales pro ha.	1909 Bales total	1910 Hectares	1910 Bales pro ha.	1910 Bales total
North Holland	1874	20.2	37864	2806	23.4	65785	2517	22.2	55872
Seeland . . .	736	28.6	21063	1131	24.1	27275	1291	26.8	34653
North Brabant	674	23.4	15775	817	23.0	18777	864	23.0	19822
Groningen . .	922	25.2	23206	2024	25.8	52259	2696	22.9	61723
Friesland. . .	22	22.3	491	50	24.2	1212	68	25.4	1726
South Holland	173	25.6	4427	276	22.6	6232	252	23.4	5906
Utrecht . . .	4	20.0	80	10	20.0	200	5	22.0	110
Total:	4405	23.3	102906	7114	24.1	171740	7693	23.3	179812

[1]) The export from Finland for the year 1898 via Åbo amounted to 61096 kg., via Kotka 29040 kg. Report of Schimmel & Co. April 1900, 8.

THE
CARAWAY DISTRICTS
of the Dutch provinces of
Zeeland, Brabant, South-and North-
Holland, Vriesland and Groningen.
Scale 1 : 2 500 000.

Caraway districts shaded
according to their importance.

	1911 Hectares	1911 Bales pro ha.	1911 Bales total	1912 Hectares	1912 Bales pro ha.	1912 Bales total	1913 Hectares	1913 Bales pro ha	1913 Bales total
North Holland	2440	24.2	64617	1068	20.7	22069	1712	21.3	36544
Seeland . . .	1268	28.3	35845	541	18.5	9990	866	22.8	19777
North Brabant	870	26.3	22870	229	17.4	3980	409	19.6	8023
Groningen . .	3329	30.9	102631	1026	19.8	20288	2273	21.0	47713
Friesland . . .	62	32.2	1996	40	19.9	797	54	23.9	1291
South Holland	252	24.2	6108	87	21.3	1852	211	21.5	4532
Utrecht . . .	9	20.0	180	—	"		2	19.0	38
Total:	8230	28.5	234247	2991	19.7	58976	5527	21.3	117918

The exports of caraway fruit from Holland amounted to: ·

1900	. . .	4092 Tons	1907	. .	6286 Tons
1901	. . .	7167 „	1908	. . .	5429 „
1902	. . .	5354 „	1909	. . .	8312 „
1903	. . .	5549 „	1910	. . .	6149 „
1904	. . .	6351 „	1911	. . .	8988 „
1905	. . .	4669 „	1912	. . .	4298 „
1906	. . .	5952 „	1913	. . .	6635 „

The price per bale of 50 kg. fluctuated between

Highest price: 24 f. in February 1908,

Lowest price: 11 f. in the summer of 1911.

Properties. Normal caraway oil is a colorless liquid which develops a yellow color in the course of time. Is has a caraway odor and a mild, spicy taste. The specific gravity lies between 0.907 and 0.918. Oils with a lower density are rare and of lesser value because of insufficient carvone content. $a_D + 70$ to $+ 80°$. Specific gravity and optical rotation are in inverse proportion; hence the angle of rotation is the higher, the lower the specific gravity. $n_{D20°} 1.484$ to 1.488. Carvone content 50 to 60 p.c. (see assay method on p. 337). In 70 p.c. alcohol oil of caraway is but sparingly soluble. With 2 to 10 vol. of 80 p.c. alcohol (crude oils sometimes yield a slightly opalescent solution) and with an equal volume of 90 p.c. alcohol it yields clear solutions.

The carvol or carvone of the caraway oil (*Oleum Carvi* of the Ph. G. IV, the fifth edition assigns the name *Oleum Carvi* to the normal oil) has a specific gravity of 0.963 to 0.966 and $a_D + 57$ to $+ 60° 30'$; $n_{D20°} 1.497$ to 1.500. The advantage of the carvone over caraway oil lies in its double strength (intensity of odor and taste), and in its more ready solubility in dilute alcohol. It is miscible with 90 p.c. alcohol in all proportions, of 70 p.c.

alcohol 1 to 2 vol. are required, and of 50 p.c. alcohol from 15 to 20 vol. are requisite for its complete solution at 20°. The solubility of carvone in 50 p.c. alcohol is a good criterion of its purity inasmuch as the presence of 2 p.c. limonene (carvene) prevents the formation of a clear solution in 20 vol. thereof.

Caraway oil and particularly carvone assume a yellow color upon standing, the oil becoming more viscid and dense. If to a solution of 1 ccm. of such a carvone in an equal volume of alcohol a few drops of a very dilute solution of ferric chloride be added, a violet color results which, however, disappears upon the addition of more reagent. The freshly distilled oil does not yield this color reaction.

Composition. In 1840 K. Völckel[1]) ascertained the presence of an oxygenated substance and of one free from oxygen. The bearer of the caraway odor, hence of the principal constituent, is oxygenated. Its composition agrees with the formula $C_{10}H_{14}O$ and was formerly designated carvol[2]). O. Wallach[3]) changed the name to *carvone* in order to express its ketone character. A good caraway oil contains 50 to 60 p.c. of carvone. Concerning its chemical properties, its constitution and derivatives, see vol. I, p. 439.

The hydrocarbon boiling at 175° and named carvene by E. Schweizer[4]), according to Wallach's[5]) investigations, is d-*limonene* (m. p. of tetrabromide 104 to 105°).

The odor of carvene obtained by fractionation differs considerably from that of pure limonene, but assumes the lemon-like odor of limonene when it is deprived of admixed carvone by treatment with phenylhydrazine acetate and shaking with a dilute solution of potassium permanganate.

Three other substances, which together constitute but 1 to 2 p.c. of the oil (one half thereof consisting of alcoholic bodies), have been found by Schimmel & Co.[6]). They are: —

[1]) Liebig's Annalen 35 (1840), 308.

[2]) *Ibidem* 85 (1853), 246. — J. H. Gladstone, Journ. Chem. Soc. 25 (1872), 1 *et seq.*; Pharmaceutical Journ. III. 2 (1872), 746; Jahresber. f. Chem. 1872, 815.

[3]) Liebig's Annalen 277 (1893), 107.

[4]) Journ. f. prakt. Chem. 24 (1841), 257.

[5]) Liebig's Annalen 227 (1885), 291.

[6]) Report of Schimmel & Co. April 1905, 19.

Fig. 25. Tying of caraway garbs (Holland).

Fig. 26. Threshing of caraway in the field (Holland).

1. A small amount of a *base*[1]) possessing a narcotic odor which was not further examined.

2. *Dihydrocarvone* with the following properties: b. p. 221° (735.5 mm.); d_{15}, 0.9297; α_D — 16°18′; n_{D20}, 1.47107. The oxime prepared according to O. Wallach and F. Kerkhoff[2]) melted at 89°. During the crystallization from alcohol it was observed that upon standing the needles which crystallize out first change into thick prisms, a change first noted by Wallach[3]). For further characterization the dibromide $C_{10}H_{15}BrO \cdot HBr$, was prepared according to Wallach[4]) by means of hydrogen bromide in glacial acetic acid and bromine. The melting point agreed with that recorded by Wallach, *viz.*, 69.5 to 70.5°.

3. *Dihydrocarveol* was isolated from fraction 94 to 97.5° (6 mm.) (d_{15}, 0.9365; α_D — 0°50′; n_{D20}, 1.48618; S.V. after acetylation 210). In order to purify the alcohol this fraction was benzoylated by means of benzoyl chloride in the presence of pyridine, the product exhausted with steam and the residue saponified. The alcohol thus obtained had the following properties: b. p. 100 to 102° (7 to 8 mm.); d_{15}, 0.9368; α_D — 6°14′; n_{D20}, 1.48364. These properties, also its odor, revealed great similarity with those of dihydrocarveol prepared from carvone; d_{15}, 0.9343; α_D + 18°0′; n_{D20}, 1.4822. Inasmuch as the phenylurethane could not be made to crystallize, the alcohol was oxidized to dihydrocarvone according to Wallach's[5]) directions with chromic acid and glacial acetic acid. Inasmuch as the oil liberated from the bisulphite compound, possessed the pure odor of dihydrocarvone, it was converted into the oxime. Recrystallized twice from alcohol, this melted at 88 to 89°. A mixture of this oxime and the oxime of *l*-dihydrocarvone likewise melted at 88 to 89°. This shows that the alcohol examined is dihydrocarveol.

According to A. Blumann and O. Zeitschel[6]), *carveol*, $C_{10}H_{15}OH$, also occurs in caraway oil.

[1]) Such bases are also found in the oils of other umbelliferous fruits such as anise oil and ajowan oil.

[2]) Liebig's Annalen 275 (1893), 116.

[3]) *Ibidem* 279 (1894), 381.

[4]) *Ibidem* 286 (1895), 127.

[5]) *Ibidem* 275 (1893), 115.

[6]) Berl. Berichte 47 (1914). 2628.

The aqueous distillate resulting during the distillation of the oil contains *acetaldehyde, methyl alcohol* (b. p.; m. p. of oxalate), *furfurol* (b. p.; m. p. of phenylhydrazone; color reactions with aniline and *p*-toluidine) and *diacetyl* (m. p. of osazone 243°; m. p. of diacetyldioxime 234.5°)[1]).

The ferric chloride reaction peculiar to old caraway oils, referred to under "Properties", is probably due to the formation of a phenol resulting from the decomposition of carvone[2]). Up to the present time, however, the proof is wanting that upon the oxidation of caraway oil by the atmosphere any phenol whatever is formed.

Formation of Caraway Oil in the Plant. In order to get some idea as to the order in which the several constituents of caraway oil are formed in the plant, Schimmel & Co.[3]) have distilled the latter in different stages of growth and examined the oils.

Oil No. 1. From the fresh plants partly in flower, partly bearing fruits; $d_{15°}$ 0.882; $\alpha_D + 65°12'$; $n_{D17°}$ 1.48306.

Oil No. 2. From the fresh plants, same as above, but after the flowers and fruits had been removed. $d_{15°}$ about 0.88 (an exact determination not made because of the small amount of material); $\alpha_D + 20°36'$; $n_{D17°}$ 1.5083.

Oil No. 3. From fresh plants after the flowering stage but before the fruits had fully matured: $d_{15°}$ 0.9154; $\alpha_D + 63°6'$; $n_{D17°}$ 1.48825.

The odor of oil No. 2 reminded but very little of caraway. It contained neither limonene nor carvone in amounts that could be detected. The small amount of oil available sufficed for a boiling temperature only. It began to boil at 195° when the thermometer rose rapidly to 230°. Between 230 and 270° about 65 to 70 p.c. of the oil came over. In the flask there remained a resinified residue.

Oils Nos. 1 and 3 are comparable in this that both were obtained from the entire plants. As to specific gravity they reveal considerable differences. The fractionation of the two oils yielded the following results: —

[1]) Report of Schimmel & Co. October 1899, 11.
[2]) Flückiger, Arch. der Pharm. 222 (1884), 362.
[3]) Report of Schimmel & Co. October 1896, 16.

	No. 1	No. 3
175 to 178°	45 p.c. }	24.1 p.c.
178 „ 185°	21 „ }	
185 „ 190°	4.5 „ }	17.8 „
190 „ 220°	5.6 „ }	
220 „ 235°	4.8 „	46.6 „
235 „ 240°	6.4 „	5.5 „
240 „ 270°	9.2 „ }	6 „
Residue and loss . .	3.5 „ }	

The distillation residue of both oils congealed to a crystalline mass. In addition to resinous products it contained a hydrocarbon which crystallized from hot alcohol in white scales that melted at 64°. It probably belongs to the paraffin series.

The difference between the two oils becomes apparent at once. Whereas in No. 1 the terpene fractions predominate and the carvone fraction is relatively small, the latter predominates in No. 3. The entire carvone fraction of the first oil yielded about 0.2 g. of pure crystalline carvoxime, thus emphasizing the low carvone content of this oil. On the other hand the carvone fractions of No. 3 supplied a good yield of carvoxime.

The result of these fractionations would, therefore, seem to indicate that the carvone content is smaller the earlier in its development the plant is distilled; it is highest in the oil distilled from mature material. For the terpene content the reverse holds true. Thus it seems probable that the plant first produces the terpene and from this the oxygenated constituent.

Both oils contain in fraction 240 to 270° a substance with a high specific gravity that is wanting in normal caraway oil. This compound, which does not possess the properties of a phenol and does not yield a color reaction with ferric chloride, has not yet been prepared in a pure state. As to its relation to the other constituents of the oil nothing whatever is known.

Examination. In commerce caraway oils are frequently met with from which the valuable carvone has been extracted in part. On the other hand we often find under the designation "carvol", oils from which only a part, but not all, of the limonene has been removed.

Such products are easily recognized by their specific gravity, which deviates from the normal. In the evaluation of carvol its solubility in 50 p.c. alcohol should likewise be considered.

The carvone content, and hence its value, of a caraway oil can be computed from its density by adopting 0.964 as the specific gravity for carvone and 0.850 as that for limonene, or more correctly as that for the non-carvone constituents of the oil. If a is the specific gravity of the oil to be examined, b the specific gravity of one of the components *(limonene)* and c the difference in the specific gravity between that of carvone (0.964) and that of limonene (0.850), the amount of the other component *(carvone)* x is obtained in percentage by means of the following equation:

$$x = \frac{(a-b)\cdot 100}{c}.$$

This assay method, which suffices completely for practical purposes, is based on the assumption, not quite correct, that carvone and limonene are the only components of the oil.

Another assumption is that the oil has not been adulterated, which, however, occurs occasionally. Thus J. Henderson [1]) describes an oil that was adulterated with castor oil. According to its density it was computed to contain 54 p. c. of carvone, but contained only 29 p.c. of this ketone. It is more exact, therefore, to resort to a carvone assay in all cases. The sulphite method (vol. I, p. 584) has proven the most satisfactory. As against the oxime method of Kremers and Schreiner (vol. I, p. 589) it has the advantage of greater accuracy and easier execution.

Alcohol is an adulterant that is often used in connection with both caraway oil and carvone. It creates the impression that the consumer has a very readily soluble oil in hand especially adapted to the manufacture of liqueurs. Hence the test for alcohol (vol. I, p. 612) should never be omitted.

702. Ajowan Oil.

Origin and Production. *Carum Ajowan,* Benth. et Hook. *(Ptychotis Ajowan,* D.C.; *Carum copticum,* Benth.) is an annual umbelliferous plant which is cultivated in India from

[1]) Pharmaceutical Journ. 82 (1909), 610.

the Punjab to Bengal and to South Deccan[1]). It also grows in Egypt, Persia and Afghanistan[2]). The brownish-gray fruits resemble those of parsley, but differ from these in their rough surface and a different odor. The ajowan fruits distilled in Europe are exclusively of Indian origin and, for the most part, enter commerce by way of Bombay. The principal market in India is said to be Marwar in Rajputana. In India the plant is known as *ajwan, ajwani, omum* or *omam.* The thymol crystals which separate from the oil are known in the bazaars as *ajwan ka-phul,* that is, flower of ajowan. Thymol, the aqueous distillate (*omum* water), also a fatty oil to which ajowan oil has been added, are used extensively in India as remedies, more particularly against cholera.

The comminuted fruits upon distillation yield 3 to 4 p.c. of oil which is used exclusively for the production of thymol. The high fat content of the exhausted and dried fruits makes them an excellent fattening fodder for cattle. They contain 15 to 17 p.c. protein and 25 to 32 p.c. of fat[3]).

Properties. Ajowan oil is an almost colorless or brownish colored liquid with a pronounced thymol odor and a sharp, burning taste, from which part of the thymol crystallizes at ordinary temperature. $d_{15°}$ 0.910 to 0.930; α_D slightly dextrogyrate to $+5°$; $n_{D20°}$ about 1.500; phenol content 45 to 57 p.c. (determined with 5 p.c. caustic soda solution); insoluble in 1 to 2.5 vol. and more of 80 p.c. alcohol.

Composition. The principal constituent, thymol (see vol. I, p. 471), was discovered almost simultaneously by R. Haines[4]) and J. Stenhouse[5]). As stated, it crystallizes in part from the oil and can be removed completely by shaking with aqueous sodium hydroxide.

[1]) G. Watt, Dictionary of the economic products of India. Calcutta 1889. vol. 2. p. 198.

[2]) J. C. Sawer, Odorographia. London 1894. vol. 2. p. 150.·

[3]) Uhlitzsch, Die landwirtschaftlichen Versuchsstationen 42 (1893), 52. — F. Honcamp u. T. Katayama, *ibidem* 67 (1907), 105. — F. Honcamp, Sächsische landwirtschaftl. Ztschr. 55 (1907), 953.

[4]) Journ. Chem. Soc. 8 (1856), 289; Jahresb. d. Chem. 1856, 622.

[5]) Liebig's Annalen 93 (1855), 269 and 98 (1856), 309.

Of the remaining portions of the oil, about one-half consists of hydrocarbons which are sold under the name "thymene" as a soap perfume.

This thymene is a mixture of cymene[1]) and several terpenes which have been examined by Schimmel & Co.[2]).

For this investigation 500 kg. of thymene were taken which were fractionated into 5 parts.

The bulk of fraction 1 boiled between 170 and 175°. In those portions which boiled between 165 and 170° the presence of *α-pinene* was demonstrated (m. p. of nitrosochloride 103 to 104°; m. p. of nitrolbenzylamine 123 to 124°). This fraction consisted principally of *p-cymene* (m. p. of hydroxy *iso*propyl benzoic acid 155 to 156°; m. p. of *p*-propenylbenzoic acid 159 to 160°). Moreover, cymene was found in all fractions of thymene.

Fraction 3 boiled between 179 and 181° and contained *dipentene* (m. p. of dihydrochloride 48 to 49°; m. p. of nitro-sochloride 104 to 105°; m. p. of nitrolpiperidide 152 to 153°).

Fraction 5 also boiled between 179 and 181'. It yielded a chloride that melted at 52°. However, this was not identical with the chloride melting at 48 to 49°, for a mixture of the two chlorides melted at the temperature of the hand. From both chlorides the hydrocarbon was regenerated by removing the hydrogen chloride with aniline. Only the hydrocarbon from the dihydrochloride melting at 48 to 49° yielded a handsomely crystallizing tetrabromide, m. p. 123 to 124°, which when mixed with dipentene tetrabromide suffered no melting point depression. The hydrocarbon obtained from the dihydrochloride melting at 52° yielded with nitrogen oxide, a terpinene nitrosite melting at 155°. Upon oxidation of the fraction with perman-ganate there resulted the erythrol, m. p. 236 to 237°, which, according to Wallach[3]), is obtained from *γ-terpinene*. Boiled with diluted sulphuric acid there resulted a mixture of phenols consisting of equal parts of thymol and carvacrol. Hence one can pass synthetically from "thymene" to thymol, the principal constituent of ajowan oil.

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[1]) Journ. Chem. Soc. 8 (1856), 289; Jahresb. d. Chem. 1856, 622.

[2]) Report of Schimmel & Co. October 1909, 14.

[3]) Liebig's Annalen 362 (1908), 308.

The terpinene nitrosite, m. p. 155°, which is characteristic for *α*-terpinene, could not be obtained directly from the fractions. Neither could a positive phellandrene test be obtained for any of the fractions. Hence phellandrene, which is a constituent of the oil from the herb, is not contained in the fruits. Of the three terpenes, *α*-pinene, dipentene, and *γ*-terpinene, the latter predominates by far.

703. Oil of Ajowan Herb.

The oil from ajowan herb has been distilled by Schimmel & Co.[1]). The yield from the fresh herb cultivated at Miltitz amounted to 0.12 p.c. The light brownish oil had a specific gravity of 0.8601 (15°) and an optical rotation of $+0°41'$. It was soluble in about 6 vol. of 90 p.c. alcohol with abundant separation of *paraffin*. As contrasted with the oil from the fruits it contained very little *thymol* (about 1 p.c.). Of the other constituents a small amount of *phellandrene* was the only one to be identified.

704. Persian Cumin Oil.

According to E. M. Holmes[2]) the Persian cumin fruits, which some time ago appeared in the London market, are derived from *Carum gracile*, Lindl. (*C. nigrum,* Royle; family *Umbelliferæ*). They are exported from Bender Abbas and Bushir[3]). In Bombay they are known as *zeerah siah* whereas the ordinary cumin fruit from *Cuminum Cyminum* is there known as *zeerah suffed.* They have been studied anatomically by C. E. Sage[4]) who supplies illustrations of the entire fruit also of the cross section with the aid of which this drug can readily be differentiated.

Upon distillation, Persian cumin yielded 2 p.c. of oil with the following properties: d 0.911; $α_D + 7°$; n 1.4980. It contained 18 p.c. of *aldehyde* (bisulphite assay) and had a more pleasant odor than ordinary cumin oil.

[1]) Report of Schimmel & Co. October 1903, 78.
[2]) Perfum. Record 4 (1913), 43.
[3]) Dipl. and Cons. Rep. London No. 3951, 1908.
[4]) Perfum. Record 4 (1913), 46.

705. Oil of Anise.
Oleum Anisi. — Anisöl. — Essence d'Anis.

Origin and Production. The anise plant, *Pimpinella Anisum*, L., family *Umbelliferæ*, comes originally from the Orient, but is now being cultivated in almost all parts of the world. The European market is supplied principally by Russia, but anise is also produced by Germany, Scandinavia, Bohemia, Moravia, France, Holland, Bulgaria, Turkey, Cyprus and Spain.

Most of the anise distilled comes from Russia where it is cultivated in the governments of Woronesh[1]) (districts of Birjutch, Ostrogoshsk and Wolniki) Kursk, Charkow, Chersson, Podolia and Tauria[2]).

A part of the crop is distilled on the spot, the remainder is either consumed as such in Russia or exported. Commercial centers for anise are Krassnoye and Alexejevka (government of Woronesh). Anise is cultivated principally by farmers[1]).

The desjatine[3]) as a rule yields 50 poods[4]), under favorable climatic conditions up to 100 poods anise fruits. If, however, it is wet during the flowering period, the yield drops as low as 20 to 25 poods: —

Anise Cultivation and Harvest in Russia from 1890 to 1913[5]).

Year	Area in desjatines	Appr. harvest in poods	Year	Area in desjatines	Appr. harvest in poods
1890	5000	150000	1902	5000	250000
1891	3700	50000	1903	5600	87000
1892	2500	22000	1904	3300	32000
1893	4000	100000	1905	4000	130000
1894	4500	140000	1906	4900	160000
1895	6000	180000	1907	5400	170000
1896	8000	240000	1908	5400	170000
1897	4500	110000	1909	4300	200000
1898	4900	160000	1910	5500	200000
1899	3700	---	1911	4600	129000
1900	4800	190000	1912	3600	110000
1901	5700	125000	1913	3300	--

[1]) Concerning the cultivation and commerce of anise in the government Woronesh a detailed account will be found in the Report of Schimmel & Co. October 1913, 22.

[2]) Comp. W. J. Kovalevski, *Die Produktivkräfte Russlands.* German edition by E. Davidson. Leipzig 1898, p 322; see also A. Bazaroff and N. Monteverte: *Die wohlriechenden Pflanzen und die ätherischen Öle,* which, however, appeared in the Russian language.

[3]) 1 Desjatine = 109,25 Ar.

[4]) 1 Pood = 16,38 kg.

[5]) Report of Schimmel & Co. October 1913, 27.

The Russian anise exported to Germany enters that country for the most part via Stettin, whereas Hamburg is the port through which Spanish and Turkish anise are imported.

Production. The anise fruits owe their odor and taste to their volatile oil content. They yield their volatile oil completely only then when they are crushed before distillation.

The following table reveals the different geographical varieties with their respective oil yields: —

Bulgarian	2.4 p.c.
Chilian	1.9 to 2.6 p.c.
Italian (Bologna)	3.5 p.c.
„ (Puglia)	2.7 to 3 p.c.
Asia Minor	2.75 p.c.
Macedonian	2.2 p.c.
Moravian	2.4 to 3.2 p.c.
Mexican	1.9 to 2.1 p.c.
East Prussian	2.4 p.c.
Russian	2.2 to 3.2 p.c.
Spanish	3.0 p.c.
Syrian	1.5 to 6.0 p.c.
Thuringian	2.4 p.c.

These rather appreciable differences are not always attributable to variations in the fruits themselves, but frequently to admixtures, intentional or unintentional, up to 30 p.c., such as stems, foreign seeds, particles of earth, small stones, &c. It is said that in Russia and Moravia earth is specially formed into particles resembling anise both as to size and color. They can be detected readily if a sample of the drug in a beaker is covered with chloroform or a concentrated solution of common salt. In this event the particles of earth remain at the bottom and the fruits rise to the surface.

The amount of inorganic admixture can be ascertained by an ash determination. Pure anise yields 7 to 10 p.c. of ash.

The exhausted anise is dried in specially constructed apparatus[1]) and is highly prized as a high-grade food for cattle on account of its protein and fat content. According to analyses made at the Agricultural Experiment Station at Möckern near

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[1]) Muspratt-Stohmann, *Technische Chemie*. IV. ed. Braunschweig 1888. vol. 1, p. 67 to 70.

Leipzig, these anise residues contain 17 to 19 p.c. protein and 16 to 22 p.c. fat[1]).

Noteworthy is the hydrogen sulphide developed during the distillation.

Properties. At slightly more than ordinary temperature (above 20°) anise oil is a colorless, strongly refractive liquid of a peculiar odor and a pure, intensely sweet taste. In the cold it congeals to a snow-white crystalline mass, which begins to melt at 15° or more and which completely liquifies at 18 or 20°. Under certain conditions the oil can be cooled considerably below its congealing point without solidifying and can remain for a long time in this condition. However, a particle of dust, contact with an anethol crystal, a violent disturbance, or scratching of the inner surface of the vessel with a glass rod cause sudden crystallization with an appreciable rise in temperature of the entire mass. The highest point on the thermometer immersed in the mass is known as the congealing point. Inasmuch as this is dependent on the anethol content of the oil, this congealing point is a valuable criterion in the evaluation of the oil. It lies between 15 and 19° and in the case of good oils not below 18°. The technique of the congealing point determination, which in the case of anise oil and anethol is preferable by far to the melting point determination on account of its accuracy, is described in detail in Vol. I, p. 563.

The specific gravity is determined for the liquid oil at 20°; $d_{20°}$ 0.980 to 0.990. Anise oil deviates the angle of polarized light slightly to the left, α_D up to $-1°50'$ (difference from fennel oil and fennel stearoptene which deviate polarized light to the right). $n_{D20°}$ 1.557 to 1.559. In order to effect complete solution with 90 p.c. alcohol $1^1/_2$ to 3 vol. are required.

From star anise oil anise oil differs only in odor and taste. The reaction with alcoholic hydrogen chloride described under Star Anise Oil, Vol. II, p. 402, does not yield reliable results.

If anise oil is exposed for longer periods to the action of light or air (more particularly in the liquid condition) its capacity

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[1]) Uhlitzsch, *Rückstände der Fabrikation ätherischer Öle.* Die landwirtschaftlichen Versuchsstationen 42 (1893), 29. — F. Honcamp, *Die Rückstände der ätherischen Ölfabrikation und ihr Wert als Futtermittel.* Sächs. landwirtschaftl. Zeitschr. 55 (1907), 953,

to crystallize is diminished[1]) and finally it will no longer con-
geal[2]). This phenomenon is attributed to the formation of oxy-
dation products (anisic aldehyde and anisic acid), also of polymers
(photoanethol, di-*p*-methoxystilbene, m.p. 214 to 215°). At the
same time the index of refraction is reduced and the specific
gravity increased. The latter can increase to such an extent
that the oil becomes heavier than water. At the same time the
oil becomes more readily soluble in 90 p.c. alcohol.

If anise oil or star anise oil or anethol (abt. 2 g.) are
evaporated in a capsule on a waterbath a comparatively high
residue, 9 to 10 p.c. of non-volatile residue is obtained. This
is viscid, odorless, no longer tastes sweet and probably consists
for the most part of photoanethol or di-*p*-methoxystilbene, a
substance, which, according to the investigations of G. de Varda[3]),
also of P. Höring and K. P. Grälert[4]) results from the action of
light on anethol[5]).

Composition. Oil of anise consists principally of two isomeric
substances $C_{10}H_{12}O$, namely, of anethol, which is solid at tem-
peratures slightly lower than ordinary, and of liquid methyl-
chavicol[6]).

Anethol, which constitutes between 80 and 90 p.c. of anise
oil is the bearer of the characteristic properties of the oil and
hence its most valuable constituent. It constitutes snow white
laminæ or flakes and melts at 22.5° to a colorless liquid which
is highly refractive, optically inactive, with a pure anise odor
and of an intensively sweet taste. Its specific gravity is 0.984
to 0.986 at 25°.

Methylchavicol is likewise optically inactive and has an
anise-like odor without, however, possessing the sweet taste of

[1]) This behavior was known as early as the beginning of the nineteenth
century and is mentioned by Hagen, *Lehrbuch der Apothekerkunst.* VI. ed.
(1806), vol. 2, p. 441.

[2]) According to E. Grimaux anethol likewise looses its capacity to
crystallise by prolonged boiling (Bull. Soc. chim. III. 15 [1896], 779).

[3]) Gazz. chim. ital. 21 (1801), I. 183; Berl. Berichte 24 (1891), Referate, 564.

[4]) Berl. Berichte 42 (1909), 1204.

[5]) Comp. Vol I, p. 476.

[6]) Report of Schimmel & Co. October 1895, 7. Bouchardat and Tardy
later verified the occurrence of methylchavicol (estragol) in Russian anise oil.
(Compt. rend. 122 [1896], 624.)

anise. The properties of methylchavicol and anethol, also their derivatives, have been described in Vol. I, pp. 475 and 476.

G. Bouchardat and E. J. Tardy[1]) claimed the presence of fenchene in anise oil. It was shown later[2]) that the anise oil examined by them had been adulterated with oil of fennel. Still later Tardy[3]) repeated his examination with unobjectionable Russian material and, like Schimmel & Co., found that fenchene is not present in anise oil.

According to Bouchardat and Tardy[2]), also Tardy[3]), *anise ketone* is another constituent of the oil. This substance they characterize as follows: a limpid liquid boiling at 263°; d_0 1.095; m. p. of semicarbazone 182°; the odor reminds somewhat of bitter almond oil. It combines with sodium acid sulphite and, when exposed to air, oxidizes to acetic acid and anisic acid. The same products result upon oxidation with potassium permanganate. For this reason Tardy assigns the formula $C_6H_4(OCH_3)CH_2COCH_3$ to the ketone.

In its properties it agrees with the *p*-methoxyphenyl acetone of A. Béhal and M. Tiffeneau[4]). The oximes of both melt at 72°. Furthermore the ketone $C_6H_4(OCH_3)CH_2COCH_3$, obtained by P. Toennies[5]) from anethol has the same boiling point, 264°, as anise ketone.

In addition to *acetaldehyde,* the first fraction of anise oil contains malodorous sulphurated products, possibly also mere traces of terpenes. In how far these substances may be attributed to impurities in the seed, which are always present, cannot be conjectured.

Adulteration and Examination. As some of the more crude adulterants observed thus far, the oils of turpentine, cedarwood, copaiba, gurjun balsam, also alcohol, spermaceti and fatty oils may be mentioned. All of these adulterants are indicated by determining the physical constants of the oil, *viz.,* specific gravity, optical rotation, solubility and congealing point.

[1]) Compt. rend. 122 (1896), 198. — Bull. Soc. chim. III. 15 (1896), 612.

[2]) Report of Schimmel & Co. April 1896, 8.

[3]) Thèse pour l'obtention du diplôme de Docteur de l'Université de Paris, p. 11 (1902).

[4]) Bull. Soc. chim. III. 25 (1901), 275.

[5]) Berl. Berichte 20 (1887), 2984.

Especially common is the cutting of anise oil with fennel oil and fennel oil stearoptene. However, even small amounts of these are detected by their dextrorotation in the polariscope. Under all circumstances dextrogyrate oils should be rejected.

In the taking of a sample for testing the oil care should be exercised to melt the oil completely and to mix it thoroughly to a homogeneous liquid.

Here also attention should once more be directed to the changes which a normal oil undergoes when carelessly kept and which have been described on p. 343 under "Properties", for these must at times be taken into account when rendering a report.

The best criterion for a good oil is its congealing point which for normal oils fluctuates between 15 and 19° and which is found mostly at about $+ 17°$.

706. Oil of Pimpinella saxifraga.

The root of pimpernel, *Pimpinella saxifraga*, L., Ger. *weiße Pimpinellwurzel* (family *Umbelliferæ*), yields 0.025 p.c. of a golden-yellow oil with a penetrating and unpleasant odor that reminds somewhat of parsley seed oil, and with a bitter, rasping taste[1]. $d_{15°}$ 0.959. It begins to boil at 240°), the thermometer rising to 300°. Above this temperature some oil still passes over but with considerable decomposition[2]).

The root of *Pimpinella nigra*, Willd., Ger. *schwarze Pimpinellwurzel*, yields 0.38 p.c. of a light blue oil that floats on water and the odor of which is less penetrating than that of the foregoing oil. Exposed to the sunlight, even in closed containers, for several weeks it becomes green[3]).

707. Oil of Sium cicutæfolium.

From the fresh herb of *Sium cicutæfolium*, Gm. (family *Umbelliferæ*) which grows in South Dakota, F. Rabak[4]) obtained 0.5 p.c. volatile oil. It was light yellow in color, had a strong odor of caraway reminding at the same time of turpentine oil.

[1]) L. F. Bley, Trommsdorff's Neues Journ. der Pharm. 12 (1826), II. 63.
[2]) Bericht von Schimmel & Co. April 1890, 37.
[3]) L. F. Bley, Trommsdorff's Neues Journ. der Pharm. 13 (1826), II. 43.
[4]) Midland Drugg. and Pharm. Review 43 (1909), 5.

With 6 vol. of 90 p.c. alcohol it yielded a turbid solution. d_{29}. 0.8447; $\alpha_D + 63°40'$; A.V. 0; E.V. 33, corresponding to 11.55 p.c. ester $C_{10}H_{17}OCOCH_3$. As contrasted with the original oil, the acetylated oil revealed no increased ester value, hence free alcohols are not present. The strong dextrorotation indicated the presence of d-*limonene*. Fuchsine solution as well as silver nitrate indicated the presence of aldehydes.

708. Oil of Seseli Bocconi.

From the umbelliferous plant *Seseli Bocconi,* Gussone (*Bubon siculus,* Spr.; *Crithmum siculum,* Boccon) L. Francesconi and E. Sernagiotto[1]) distilled 0.295 p.c. of a volatile oil with a density of 0.8475 (27´). l-*Pinene* and *β-phellandrene* appear to be the principal constituents of the oil. The roots contain but little oil.

709. Samphire Oil.

FRENCH OIL.

The several parts of the plant of *Crithmum maritimum*, L., Ger. *Seefenchel* (family *Umbelliferæ*), were distilled by F. Borde[2]). Of material collected during the first part of August, after flowering had about ceased, the leaves and stems yielded 0.3 p.c., the fruits 0.7 p.c. of oil; the same material collected during the second half of August yielded 0.15 and 0.8 p.c. respectively, and that collected about the middle of September 0.154 and 0.7 p.c. respectively. The oil distilled from the leaves and stems was denser than that from the fruits; it is of a dark yellow color and possesses an aromatic, pungent odor reminding of the plant. The crushed fruits yield a light yellow oil, which, if the fruit is distilled after having been dried, has a pleasant odor.

Oil from leaves and stems: d_4. 1.0374 to 1.0519; α_D^3) 6°42' to 8°15'. Oil from fresh fruits: d_4. 0.9661 to 0.9730; α_D^3) 5°27' to 6°12'. Oil from the dried fruits: d_4. 0.9581; α_D^3) 8°9'.

[1]) Atti R. Accad. dei Lincei, Roma (5), 20, II. (1911), 481; Chem. Zentralbl. 1912, I. 422.

[2]) Bull. Sciences pharmacol. 16 (1909), 132; Chem. Zentralbl. 1909, I. 1566. — Older literature: G. Lavini and H. Herouard, Mem. della Reale Acc. delle Scienze di Torino 25, 13; Journ. de Pharm. et Chim. IV. 3 (1866), 324.

[3]) The sign (+ or —) is wanting in the original.

According to M. Delépine[1]) the French oil contains d-*pinene* (m.p. of terpin hydrate 116°, m.p. of pinene hydrochloride 130°), *dipentene* (m.p. of nitrolpiperidine 152°) and *p*-cymene (m.p. of *p*-hydroxy*iso*propylbenzoic acid 157°; m.p. of *p*-toluic acid 177°).

In fraction 210 to 214° Delépine found *thymol methyl ether,* a substance which had not previously been found in a volatile oil, neither were other ethers known to occur, whereas those of carvacrol occur frequently. By treating this methyl ether with hydrogen bromide in glacial acetic acid solution he obtained thymol. In addition this fraction contains small amounts of other substances: *phenols,* a *high-molecular fatty acid,* and an *alcohol* that has the odor of roses, which, however, could not be investigated because of the small amount available.

As principal constituent of the oil Delépine[2]) identified *dill-apiol* with the following constants: b.p. 294 to 295° (corr.) with slight decomposition, 157 to 158° (corr.) (under 13 mm. pressure); $d_4^{13°}$ 1.1644; $n_{D25°}$ 1.52778; mol. refr. found 59.20, computed 58.28. For better characterization he prepared the tribromide, $C_{12}H_{13}BrO_4Br_2$ melting at 110°. By heating the dillapiol with sodium ethylate he converted it into the dill *iso*apiol melting at 44°. By oxidizing the dillapiol with iodine and mercuric oxide he obtained dimethoxy-2,3-methylene-dioxy-4,5-hydratropic aldehyde, $C_9H_9O_4 \cdot CH(CH_3)CHO$, a liquid that boils at 189° (17 mm. pressure) with the following properties: $d_4^{13°}$ 1.2407; $n_{D25°}$ 1.53191; mol. refr. found 59.79, computed 58.96; m.p. of the oxime 102°; m.p. of semicarbazone 148°. When oxidized with silver oxide the corresponding acid, $C_9H_9O_4 \cdot CH(CH_3)CO_2H$, resulted which melted at 119°.

Inasmuch as the oil contains 40 to 60 p.c. of dillapiol, it affords a cheap and abundant first material for the production of this heretofore difficultly available compound.

The physiological action of the oil has been studied by J. Chevalier[3]).

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[1]) Compt. rend. 150 (1910), 1061. — Bull. Soc. chim. IV. 7 (1910), 468.

[2]) Compt. rend. 149 (1909), 215. — Comp. also F. Borde, *Etude pharmacognostique du Crithmum maritimum L.* Lons-le-Saunier 1910.

[3]) Compt. rend. des séances de la Soc. de Biologie 68 (1910), 306; Report of Schimmel & Co. October 1910, 113.

ITALIAN OIL.

Different from the French in composition is the Italian oil which has been investigated by L. Francesconi and E. Sernagiotto[1]). The oil, obtained in the island of Sardinia by distillation of the entire plant, was reddish-yellow, had a parsley-like odor and showed a slightly acid reaction. The yield (from fresh herb?) amounted to 0.16 p.c.; d_{20}, 0.9816; $[\alpha]_D + 3.18°$; n_D 1.4978; S.V. 6.5; E.V. after acetylation 11.24. Upon slow steam distillation the oil was separated into a readily volatile portion (d 0.8611) and a difficultly volatile portion (d 1.1463). From the latter a *paraffin* m.p. 63° separated upon cooling. The balance consisted of *dillapiol*. Judging from its optical constants, the more volatile portion consisted principally of monocyclic terpenes with two double bonds. The leaf oil was the richest in these constituents.

The most volatile fraction, when treated, in glacial acetic acid solution, with nitrosylchloride, yielded β-phellandrene nitrosochloride, as was proven by its conversion into $\Delta^{1.5}$-dihydrocuminic aldehyde. The β-phellandrene is to be found in the first fractions only.

In the higher-boiling, inactive portions, more particularly in those boiling at 113 to 115° (30 mm.) a hitherto unknown terpene has been found which the authors name *crithmene*. It has the following properties: b.p. 178 to 180 (759 mm); d_{12}, 0.8679; n_D 1.4806. It yields an α-nitrosochloride melting at 103 to 104°. In addition crithmene yields a nitrosite (m.p. 89 to 90°) and a nitrosate (m.p. 104 to 105°). When crithmene nitrosochloride is decomposed with alcoholic potassa there results a nitrogenous substance free from chlorine melting at 131°, also a nitrogenous substance melting at 53 to 54°. By passing hydrogen

$$C:CH_2$$
$$H_2C \diagup \diagdown CH_2$$
$$H_2C \diagdown \diagup CH_2$$
$$C:C(CH_3)_2$$

Crithmene.

chloride into a glacial acetic acid solution of crithmene, *trans*-terpinene dihydrochloride resulted thus revealing it as a derivative of *p*-cymene. It is inactive but not a racemic mixture, hence the presence of asymmetric combinations in the crithmene molecule would seem excluded. Comparing crithmene and its derivatives with the other terpenes and their derivatives, Francesconi and
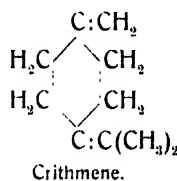
[1]) Atti R. Accad. dei Lincei, Roma (5), 22, I. (1913), 231, 312, 382; Chem. Zentralbl. 1913, I. 1685, 1686, 1687.

Sernagiotto arrive at the conclusion that crithmene is $\Delta^{1(7),4(8)}$- p-menthadiene of the formula reproduced above.

p-*Cymene* also occurs in the Sardinian oil.

710. Oil of Fennel.

Oleum Fœniculi. — Fenchelöl. — Essence de Fenouil.

Origin. Fennel, *Fœniculum vulgare*, G. (*F. capillaceum*, Gilibert; *Anethum Fœniculum*, L.) is a stately umbelliferous plant which is cultivated on account of its edible root, but more particularly on account of its fruits, in Germany (around Lützen), Moravia, Galicia, Bukovina, Moldavia, Roumania, Bessarabia, Podolia, Macedonia, France, Italy, India, Japan, and many other countries. The area that supplies most of the fennel for distillation is the border territory of Galicia, Bukovina, Moldavia, Bessarabia and Podolia. For Roumania and Southern Russia, Novo Seliza on the Pruth is the shipping point, for Southern Galicia Skala on the Zbrucz, a tributary of the Dnieper. The fruits of these several countries differ greatly not only in their exterior appearance[1]), structure[2]), size, and color, but also as to the composition of the oils distilled from them. These differences are so great that they are possibly unequalled by those of the varieties of any other plant.

The oil distilled from the Lützen, Roumanian, Galician, Moravian and Japanese fennel is characterized by the bitter-tasting fenchone, which, together with the anethol, causes the characteristic odor of fennel. Fenchone is wanting in the sweet or Roman (French) and in Macedonian fennel. On the other hand anethol is contained in traces only or not at all in the wild bitter fennel.

In the several fennel oils the most varying terpenes are found. The Lützen fennel contains pinene and dipentene, wild bitter fennel phellandrene and Macedonian fennel limonene. Thus it becomes apparent that under the designation fennel oil products of very different properties are comprised.

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[1]) Descriptions, with illustrations, of the several kinds of commercial fennel are given by J. C. Umney: The commercial varieties of fennel and their essential oils. Pharmaceutical Journ. 58 (1897), 225.

[2]) Comp. C. Hartwich and A. Jama, *Beiträge zur Kenntnis des Fenchels*. Berichte d. deutsch. pharm. Ges. 19 (1909), 396.

In the following account the designation Oil of fennel is restricted to the *Oleum Fœniculi* of the German Pharmacopœia, the ordinary fennel oil of commerce, such as is obtained from the distillation of Lützen, Roumanian, Moravian and Galician fennel.

Production. The yield depends largely upon the purity of the fruits. This is particularly influenced by added earthy material, which in the case of the Galician drug sometimes amounts to more than 30 p.c. The adulteration with the fruits of *Meum athamanticum,* Jacq. pointed out by C. Hartwich and A. Jama[1]) is not likely to occur in the wholesale trade.

The principal commercial varieties, when crushed, afford the following oil yields: —

1. Saxon fennel (Lützen) . . yield 4.4 to 5.5 p.c.
2. Galician „ . . . . . „ 4 „ 6 „
3. Moravian „ . . . . . „ 3 „
4. Roumanian fennel . . . „ 4.6 „

The distillation residues are a valuable fodder for animals. (See oil of caraway p. 328.) When dried they contain 14 to 22 p.c. of protein and 12 to 18.5 p.c. of fat.[2])

Properties. At average temperature oil of fennel constitutes a colorless or faintly yellowish liquid possessing a peculiar fennel odor and a taste which at first is bitter and camphor-like, but afterward sweet. $d_{15°}$ 0.965 to 0.977; α_{1}, $+11$ to $+20°$, rarely up to $+24°$: $n_{D20°}$ 1.528 to 1.538. The congealing point of a good fennel oil, which is determined as described in Vol. I, p. 563, does not lie below $+5°$ (if the oil has·been subcooled to $+3$") and rises to $+10°$. With poorer qualities $+3°$ may be regarded as the lower limit of the congealing point. The oil is soluble in 5 to 8 vol. of 80 p.c. alcohol (occasionally with slight turbidity), and in 0.5 vol. of 90 p.c. alcohol.

Composition. *Anethol*[3]), which crystallizes out in the cold is the constituent longest known (see Vol. I, p. 476). Oils of good quality contain about 50 to 60 p.c. of this substance. Characteristic

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[1]) Comp. C. Hartwich and A. Jama, *Beiträge zur Kenntnis des Fenchels.* Berichte d. deutsch. pharm. Ges. **19** (1909), 403.

[2]) Uhlitzsch, Die landwirtschaftlichen Versuchsstationen **42** (1893), 36. — F. Honcamp, *Die Rückstände der ätherischen Ölfabrikation und ihr Wert als Futtermittel.* Sächs. landwirtschaftl. Zeitschr. **55** (1907), 953.

[3]) Details may be found under History of fennel oil in vol. I, p. 174.

for the oil is a second compound, contained in fraction 190 to
192°, with its intensely bitter and taste of camphor[1]). According
to the investigations of O. Wallach and F. Hartmann[2]) it is a
ketone. Originally it had been named fenchol, but later was
designated *fenchone*. Its properties and derivatives have been
described in Vol. I, p. 458.

Of terpenes ordinary fennel oil contains d-*pinene, camphene,
α-phellandrene* and *dipentene*. Pinene was identified in fraction
157 to 160° ($α_D$ | 41°58′) by its nitrosochloride and nitrol-
benzylamine m.p. 122°[1])[3]).

A fraction with similar boiling point was used for the
identification of *camphene*[3]). Upon hydration by means of glacial
acetic acid + sulphuric acid, a yellowish oil resulted with the
odor of *iso*bornylacetate. Under 12 mm. pressure it distilled
over, for the most part, between 62 and 108° (the bulk at 65°).
Saponification of those portions that passed over above 95° with
alcoholic potassa and distillation of the saponification reaction
mixture with water vapor, yielded a colorless crystalline mass
which possessed the odor of *iso*borneol, and which, after four
or five recrystallizations from petroleum ether, melted at 208 to
208.5°. It was impossible to cause the *iso*borneol to melt higher.

Phellandrene was found in a fraction with the following
constants: $d_{16.5°}$ 0.8733; $α_D$ + 34°34′; $n_{D22.9°}$ 1.47186; b.p. 49.2 to
55° (7 mm.). The crude nitrite, obtained with a rather poor yield,
was deprived of its grossest impurities by triturating it with a
cold mixture of methyl alcohol and ether, and then recrystallized
from acetic ether. Repeated crystallization yielded the α-nitrite
of α-*phellandrene*, which resulted in fine colorless needles,
m.p. 114° (when heated slowly) or 119° (when heated quickly).
The specific angle of rotation of this nitrite in chloroform solu-
tion was found to be $[α]_D$ — 133.4°.

From the mother liquors of the α-nitrite the β-nitrite of
α-phellandrene was precipitated with 60 p.c. alcohol. Upon
resolution in acetic ether and reprecipitation and frequent
repetition of these processes the β-nitrite of α-phellandrene was

[1]) Bericht von Schimmel & Co. April 1890, 20.
[2]) Liebig's Annalen 259 (1890), 324 and 263 (1891), 129.
[3]) Report of Schimmel & Co. April 1906, 37.

obtained in felty needles grouped in stellar formation, which melted at 103 to 104° but were not pure. Nevertheless the dextrorotation of the nitrite in chloroform solution was established, $[\alpha]_D + 16.3°$.

After ten fractionations a fraction boiling at 180 was obtained which, when shaken with hydrogen bromide in glacial acetic acid solution, yielded *dipentene* dihydrobromide melting at 94°, and upon bromination dipentene tetrabromide [1])[2]) melting at 123 to 124°.

E. Tardy[3]) claimed the presence of cymene without, however, supplying sufficient proof. Schimmel & Co.[2]) have demonstrated that it is not a constituent of fennel oil.

The fraction which ought to have contained cymene (b.p. 176.2 to 180.5° [762 mm]; $\alpha_D + 23°56'$) was oxidized with cold 1 p.c. permanganate solution. In order to remove the fenchone, which cannot be gotten rid of by oxidation, from this fraction it was converted into the oxime melting at 161° whereupon the hydrocarbons were separated from the fenchone oxime by steam distillation. The yellowish oil which passed over was then oxidized farther with 1 p.c. permanganate whereby the optical rotation was gradually reduced. Of the 76 g. of oil used there finally remained but 2.5 g., the α_D of which was + 12°10'. This oily residue was heated with a solution of 5.04 g. of potassium permanganate in 140 g. water on a water bath. The oxidation, however, failed to yield either *p*-hydroxy*iso*propyl benzoic acid, a characteristic derivative of cymene, or terephthalic acid. Only a very small amount of a brownish-yellow oil, which could not be characterized any farther resulted from this reaction. Hence *p*-cymene does not occur in fennel oil.

According to Tardy[4]) fennel oil also contains *methyl chavicol* (b.p. 213 to 215°; anisic acid; rearrangement to crystallizable anethol), and anise ketone[5]). To this Tardy assigns the formula $CH_3O \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot CH_3$. It boils between 260 and 265°, yields a solid compound with acid sulphite and is oxidized to anisic acid and acetic acid. The semicarbazone melts at 182°.

[1]) Bericht von Schimmel & Co. April 1890, 20.
[2]) Report of Schimmel & Co. April 1906, 38.
[3]) Bull. Soc. chim. III. 17 (1897), 660.
[4]) *Loc. cit.*
[5]) See also under anise oil, p. 345.

In the first fractions of fennel oil are to be found *aldehydes*, also traces of a *basic* constituent which has a disagreeable pyridine-like odor, yields a faint pyrrol reaction, also a platinum double salt difficultly soluble in water[1]).

Anisic aldehyde and *anisic acid,* the oxidation products of anethol that are found in every anethol-containing oil, have likewise been detected in oil of fennel.

Examination. Special attention should be directed to oils which have been deprived of part of their anethol by fractionation or freezing. The congealing point of such oils lies below $+3°$, which is the lowest permissible limit. Alcohol, the presence of which has been observed occasionally, becomes noticeable through the lowering of the specific gravity, as does also the addition of turpentine.

Two oils which had been deprived of most of their anethol by freezing, showed the following properties: d_{15}. 0.9543 and 0.9381; $\alpha_D + 26°33'$ and $+24°45'$; n_{D20}. 1.50930 and 1,50939; congealing point $-15°$ and $-5.5°$.

So-called light fennel oil, *i. e.,* fennel oil that has been freed of its anethol content by freezing or fractionation is apt to fall within the following constant limits: d_{15}. 0.884 to 0.955; $\alpha_D + 42$ to $51°$; soluble in 1 to 7 vol. and more of 80 p.c. alcohol. The richer such an oil is in fenchone, the greater both density and optical rotation.

In order to ascertain the changes that result in the congealing point from an increasing anethol content, 5, 10, 15 and 20 p.c. of anethol were added to an oil.

Fennel oil			cooled to $+3°$, Cong. pt. 5.25°[2])	Difference
"	" $+$ 5 p.c. anethol "	" $+3°$, " " 6.1°		0.85°
"	" $+10$ " " " " $+3°$, " " 6.6°			1.35°
"	" $+15$ " " " . " $+3°$, " " 7.4°			2.15°
"	" $+20$ " " " " $+3°$, " " 8.0°			2.75°

In judging a fennel oil its age and the conditions of storage must be taken into consideration for oxidation and polymerization phenomena[3]) cause no inconsiderable changes, more particularly

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[1]) Report of Schimmel & Co. April 1906, 37.

[2]) The same oil cooled to about $-0,5°$ congealed at about 4,5°.

[3]) Comp. Report of Schimmel & Co. October 1904, 42 and November 1906, 70.

in the specific gravity and congealing point. (See analogous changes produced in anise oil as described on p. 344.)

The fennel oils hereinafter described are of scientific rather than practical interest.

OIL FROM SWEET OR ROMAN FENNEL.

The variety of fennel, formerly differentiated as *Fœniculum dulce,* D.C. which is cultivated in southern France yields 2 to 3 p.c. of oil upon distillation. It is characterized by its high anethol content and the absence of fenchone. $d_{15°}$ 0.976 to 0.980[1]); $\alpha_D + 5°$ to $+ 16° 30'$[3]); congealing point $+ 10$ to $+ 14.5°$.

· OIL FROM MACEDONIAN FENNEL.

This oil closely resembles the sweet fennel oil. It has a pure sweetish taste and a high anethol content. Yield 1.7 to 3.8 p.c. $d_{15°}$ 0.970 to 0.980; α_D ¦ 5 to ¦ 12°; congealing point $+ 7$ to $+ 12°$.

Fenchone is absolutely wanting in Macedonian fennel oil. The terpenes boil between 170 to 180°. With glacial acetic acid and sodium nitrite fraction 170 to 175° ($\alpha_D + 57° 53'$) yielded a slight but distinct *phellandrene* reaction. Upon bromination fraction 175 to 180° ($\alpha_D + 64° 33'$) yielded *limonene* tetrabromide melting at 104 to 105°. Hence the oil contains *d*-phellandrene and *d*-limonene[2]).

OIL FROM THE WILDGROWING BITTER FENNEL.

The bitter fennel which grows wild in France, Spain and Algiers, yields upon distillation about 4 p.c. of volatile oil; $d_{15°}$ 0.905 to 0.925; $\alpha_D + 40$ to 68°.

The principal constituent of bitter fennel oil is a terpene discovered by A. Cahours[3]) and more closely examined by N. Bunge[4]), which O. Wallach[5]) recognized as d-*α-phellandrene*. The higher-boiling fractions taste slightly bitter, hence may be

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[1]) J. C. Umney, Pharmaceutical Journ. 58 (1897), 226.
[2]) Observations made in the laboratory of Schimmel & Co.
[3]) Liebig's Annalen 41 (1842), 74.
[4]) Zeitschr. f. Chemie 5 (1869), 579.
[5]) Liebig's Annalen 239 (1887), 40.

regarded as containing some fenchone. Anethol is either not present at all or in but small amount.

E. Tardy[1]) has found in French bitter fennel oil a crystalline compound melting at 213°. He suspects that it may be a coumarin-like compound which has resulted from the action of anisic aldehyde or anisic and acetic acids. Probably it is nothing more or less than *di-p-methoxy stilbene*, m. p. 214 to 215°, which results when anise oil is exposed to light (see p. 344).

Upon fractionation of a larger quantity of French bitter fennel oil Schimmel & Co.[2]) observed that fine crystals separated from the higher fractions as well as from the residue. These crystals were readily deprived of adhering oil by washing with petroleum ether, and after recrystallization from acetic ether were obtained in white, broad needles. From alcohol they crystallized in stunted, bold crystals melting at 164 to 165°.

Oil from Chinese Fennel.

The fruits of Chinese fennel have been described in detail by L. Rosenthaler[3]), who obtained, upon distillation, 3.34 p.c. of oil, concerning which nothing more is known.

Oil from Indian Fennel.

This oil is distilled from the variety known as *Fœniculum Panmorium*, D. C. The yield is 0.72[4]) to 1.2 p.c.; $d_{15°}$ 0.968[4]) to 0.973; α_{D} + 21°[4]); m. p. 18.2°[4]). It contains *fenchone* and *anethol*.

Oil from Japanese Fennel.

Japanese fennel is recognized by the smallness of the fruits, which, in commerce, are also known as Japanese anise. The oil closely resembles the German fennel oil. Yield 1.8 to 2.7 p.c.[5]); $d_{15°}$ 0.968 to 0.976; α_{D} + 10°) to + 16°; congealing point + 9°. The oil contains *fenchone* and *anethol*.

[1]) Bull. Soc. chim. III. 17 (1897), 661.
[2]) Report of Schimmel & Co. April 1901, 13.
[3]) Berichte d. deutsch. pharm. Ges. 23 (1913), 576.
[4]) J. C. Umney, Pharmaceutical Journ. 58 (1897), 226.
[5]) J. C. Umney, *ibidem* 57 (1896), 91.
[6]) Report of Schimmel & Co. October 1893, 50.

OIL FROM SICILIAN ASS'S FENNEL.

The fruits of *Fœniculum piperitum*, D. C. *(Finocchio d'asino,* Ger. *Esels-Fenchel)* have a pungent taste and are used as a spice in southern Italy. Upon distillation they yield 2.9 p.c. of oil; d 0.951. It can contain only traces of anethol for, even when cooled to − 5°, no separation took place.

OIL FROM FENNEL OF ASIA MINOR[1].

Yield 0.75 p.c.; $d_{15°}$ 0.987.

OIL FROM SYRIAN FENNEL[1].

Yield 1.6 p.c.; $d_{15°}$ 0.972.

OIL FROM PERSIAN FENNEL.

Yield 1.7[2]) to 1.9[3]) p.c.; $d_{15°}$ 0.976[3]) to 0.977[2]); $α_D$ + 7°[4]) to + 14°[2]); congealing point about + 11°.

OIL FROM RUSSIAN FENNEL[3].

Yield 4.8 p.c.; $d_{15°}$ 0.967; $α_D$ + 23°; m. p. + 4.4°.

OIL FROM ALGERIAN FENNEL.

An oil of Algerian bitter fennel, examined by E. Tardy[4], had the following constants: d_0 0.991; $α_D$ + 62 16′. Of its constituents the following were identified: *pinene, phellandrene* (m. p. of nitrite 102°), *fenchone, methyl chavicol, anethol,* a *sesquiterpene,* and a small amount of a substance $C_{10}H_{14}O_2$ which in all probability is *thymohydroquinone*. It melts at 138 to 140°, is soluble in hot potassium hydroxide solution and is again precipitated from this solution by acids. The crystals thus obtained melt at 184°. Oxidized with bichromate and sulphuric acid a substance melting at 45° resulted. Tardy concludes that the substance is identical with thymohydroquinone which melts at 145° and upon oxidation yields thymoquinone which melts at 48°. The crystals obtained from the hot potassa solution correspond

[1]) Report of Schimmel & Co. April 1897, table, appendix, p. 20.

[2]) J. C. Umney, Pharmaceutical Journ. 58 (1897), 226.

[3]) Observations made in the laboratory of Schimmel & Co.

[4]) *Etude analytique sur quelques essences du genre anisique. Thèse,* Paris 1902, p. 23.

to hydroxythymoquinone, which melts at $187°$ and is obtainable on treating monobromothymoquinone with hot potassa solution.

711. Oil of Fennel Herb.

The properties of an oil distilled by Carthaus in Java from the stems and leaves of *Fœniculum capillaceum*, Gilibert, are recorded in the Annual Reports of Buitenzorg for the year 1906[1]); $d_{20°} 0.970$; $\alpha_{D20°} + 4°50'$; congealing point $+ 12.8°$. The bulk of the oil passes over between 227 and $235°$.

For several oils of like origin the following properties were ascertained in the laboratory of Schimmel & Co.[2]); $d_{15°} 0.970$ to 0.984; $\alpha_D + 5°34'$ to $+ 21°40'$; congealing point $+ 4°$ to $+ 16.2°$. The composition of the Javanese herb oil seems to correspond closely to the fennel (seed) oil of commerce.

An oil distilled from the herb of *Fœniculum capillaceum*, Gilibert in the Norman Island of Jersey[3]) constituted a colorless liquid with an esdragon-like odor. It was soluble in 5 vol. and more of 80 p. c. alcohol with slight turbidity; $d_{15°} 0.9561$; $\alpha_D + 16°40'$. *Anethol* is present in small amount only. Judging from its odor *methylchavicol* is an important constituent.

712. Oil of Water-Fennel.

Oleum Phellandrii Aquatici. — Wasserfenchelöl. — Essence de Fenouil d'Eau.

Origin and Production. The fruits of water-fennel, *Oenanthe Phellandrium*, Lam. (*Oenanthe aquatica*, Lam., *Phellandrium aquaticum*, L.) contain 1 to 2.5 p.c. of volatile oil. Water-fennel oil is at first colorless or of a wine-yellow color which later becomes darker. It has a strong penetrating odor and a burning taste; $d_{15°} 0.85$ to 0.89; $\alpha_D + 12°42'$ to $+ 19°$; $n_{D20°} 1.484$ to 1.495. It begins to boil at about $170°$ and up to $172°$ 50 to 60 p.c. pass over. The thermometer gradually rises to $300°$ and finally a black residue remains in the distilling flask[4]). In connection with the distillation of water-fennel H. Haensel[5])

[1]) Jaarb. dep. Landb. in Ned.-Indië, Batavia **1907**, 45.

[2]) Comp. Report of Schimmel & Co. November **1908**, 71.

[3]) *Ibidem* April **1913**, 111.

[4]) C. Bauer, *Über das ätherische Öl von Phellandrium aquaticum. Inaug.-Dissert.* Freiburg 1885.

[5]) Pharm. Ztg. **43** (1898), 760.

observed the separation of a small amount of heavy oil at the bottom of the Florentine flask.

Composition. As was shown by L. Pesci [1]) the oil consists of 80 p.c. of a terpene which is characterized by a nitrite melting at 103°. It was named *phellandrene* from the plant which had yielded the oil. Later it was learned that this hydrocarbon occurs in two modifications, the one· occurring in the water-fennel oil being the *d-β*-phellandrene. (For properties and derivatives see Vol. I, p. 325.)

During their investigation of the chlorides obtained from the β-phellandrene of water-fennel oil, I. Kondakov and J. Schindelmeiser [2]) found *pinene* hydrochloride, the formation of which is attributable to pinene contained in the oil. O. Wallach [3]) further regards the presence of *sabinene* in water-fennel oil as not impossible.

The fractions boiling higher than phellandrene contain an aldehyde $C_{10}H_{16}O$, named *phellandral,* which was discovered by Schimmel & Co. [4]) and the odor of which reminds vividly of that of cuminic aldehyde. Its structural formula, also its properties and derivatives are recorded in Vol. I, p. 432.

From those portions which did not react with acid sulphite careful fractionation isolated an alcohol named *androl* [1]) which had the following properties: b.p. 197 to 198°; $d_{16°}$ 0.858; a_D · 7° 10′; $n_{D20°}$ 1.44991. It possesses the characteristic odor of water-fennel oil to a high degree, hence appears to be the principal bearer of this odor. With carbanil a phenyl urethane resulted which, after recrystallization from alcohol, melted at 42 to 43°. Its analysis would seem to indicate that the formula $C_{10}H_{20}O$ should be assigned to the underlying androl. Upon oxidation it yielded neither an aldehyde nor a ketone.

With the aid of phthalic acid anhydride an *alcohol* with a rose-like odor could be isolated from the fraction boiling about 230°. Its diphenylurethane, after one crystallization from alcohol, melted at 87 to 90°. The amount·was too small for further investigation.

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[1]) Gazz. chim. ital. 16 (1886), 225.

[2]) Journ. f. prakt. Chem. II. 75 (1907), 141.

[3]) *Terpene und Campher.* II. ed. Leipzig 1914. p. 485, footnote.

[4]) Report of Schimmel & Co. October 1904, 88; October 1905, 71.

713. Oil of Oenanthe crocata.

From the exceedingly poisonous umbelliferous *Oenanthe crocata*, L., which is common in England, F. Tutin[1]) prepared an alcoholic extract which, upon distillation with water vapor, yielded 0.1 p.c. of oil computed with reference to the dry herb. It was light yellow in color and of an odor that was not pleasant; $d_{15°}$ 0.9381; optical rotation $+1°16'$ in a 2.5 cm. tube. Under 100 mm. pressure it boiled between 100 and 200°, the largest part going over between 180 and 200°. The oil contained *furfurol*.

714. Oil of Aethusa Cynapium.

From the air-dried herb of *Aethusa Cynapium*, L. (Ger. *Hundspetersilie*) F. B. Power and F. Tutin[2]) prepared an alcoholic extract which, upon evaporation of the solvent, was distilled with water vapor. The oil yield was 0.015 p.c. computed with reference to the fresh herb. At first colorless, it soon assumed a dark brown color and had an unpleasant odor. The aqueous distillate contained formic acid. The distillation residue (0.8 p.c. computed with reference to the fresh plant) was partly soluble in petroleum ether. After saponification of the dissolved part there were isolated *pentatriacontane* $C_{35}H_{72}$ (m.p. 74°), an *alcohol* (m.p. 140 to 141°; $[\alpha]_D$ -35.7°) isomeric with phytosterol, $C_{26}H_{44}O$, or a lower homologue. The saponification liquid contained *formic* and *butyric acids*. The portion insoluble in petroleum ether yielded formic, butyric and protocatechuic acids upon fusion with alkali.

715. Oil of Bald-money.

OIL FROM THE ROOT. The dried roots of *Meum athamanticum*, Jack., Ger. *Bärwurz*, yielded upon distillation 0.67 p.c. of a dark yellow oil which greatly resembled that of lovage as to odor. At ordinary temperature it is viscid or solid; $d_{21°}$ 0.999 and $d_{30°}$ 0.8971. It begins to boil at 170°. Above 300° greenish-blue fractions having a celery-like odor were obtained. During this fractionation about one-half of the oil resinified[3]).

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[1]) Pharmaceutical Journ. 87 (1911), 296.

[2]) Journ. Soc. Chem. Industry 24 (1905), 938.

[3]) Bericht von Schimmel & Co. April 1889, 43.

OIL FROM THE HERB. Herb collected in the vicinity of St. Andreasberg in the Harz mountains yielded upon distillation 0.88 p.c. of a dark reddish-brown oil that possessed a celery-like odor[1]). It was soluble in 3 vol. of 90 p.c. alcohol; d_{15} 0.9053; $n_{D20°}$ 1.50327; A.V. 8.8; E.V. 63.1. On account of the dark color the optical rotation could not be ascertained. There separated from the oil white crystals which melted at 83 to 84°, but after one recrystallization from alcohol at 91°, and which are probably identical with guajol.

716. Oil of Silaus pratensis.

The fruits[2]) of the wild umbelliferous *Silaus pratensis*, Besser, growing in Germany, yielded 1.4 p.c. of oil upon distillation, the odor of which reminded distinctly of esdragon. d_{15} 0.982; $a + 0°7'$; S.V. 20.8. In the cold it separates a *stearoptene* consisting of fine needles.

717. Oil of Lovage.

Oleum Levistici. — Liebstockwurzelöl. — Essence de Livèche.

Origin. All parts of *Levisticum officinale*, Koch *(Angelica Levisticum*, Baillon, *Ligusticum Levisticum*, L., Ger. *Liebstock)*, which is cultivated as a medicinal plant, have a decided aromatic odor and contain volatile oil. Formerly this was distilled only from the roots, more recently it is also obtained from fruits and herb.

Production. When perfectly fresh, the aromatic roots of lovage yield upon distillation with water vapor 0.1 to 0.2 p.c.; when wilted 0.3 to 0.6; dry 0.6 to 1 p.c. of oil, the odor of which resembles angelica oil. Yellow or brown oils are obtained according to the character of the root, the former from fresh, the latter from dry roots. These oils show but a slight difference in specific gravity but behave differently upon distillation[3]). The distillation of dry lovage yields from the beginning, but more particularly toward the end, a yellow, sticky, resinous mass, some of which adheres to the condenser tube, the bulk

[1]) Report of Schimmel & Co. April 1913, 111.
[2]) *Ibidem* October 1895, 65.
[3]) *Ibidem* April 1895, 9.

of which, however, remains dissolved in the oil. When the green root is distilled, scarcely any of this resin is observed. If the root is distilled immediately when harvested, this resinous film is not observed at all. If the oil from green root is rectified, practically the entire oil is volatile; oil from dry root, however, leaves a large amount of resin.

Properties. $d_{15°}$ 1.00 to 1.049; α_D inactive or slightly dextrogyrate (up to $+6°$)[1]); $n_{D20°}$ 1.539 to 1.552; soluble in 2 to 3.5 vol. of 80 p.c. alcohol, yielding a clear or slightly turbid solution. A.V. 2 to 10; E.V. 175 to 230; E.V. after acetylation (one determination) 227.8[2]). The higher ester number of lovage oil does not appear to be due to an ester but to a lactone-like compound, about which, however, nothing is known thus far.

Composition. If the oil, which has been saponified with alcoholic potassa, is distilled with water vapor and the oil thus obtained subjected to fractionation *in vacuo*, there results, according to R. Braun[3]), a fraction boiling at 176° (air pressure) of the composition of a terpene ($d_{15°}$ 0.8534; $\alpha_D + 5°$). As a principal fraction Schimmel & Co.[4]) isolated a liquid which boiled between 107 and 115° (15 mm.) from which distillation under ordinary pressure yielded a fraction boiling at 217 to 218°. Upon cooling this congealed to a crystalline mass and revealed all of the properties of d-α-*terpineol;* α_D (in the superfused condition) $+79°18'$ at 22° (m.p. of terpinylphenylurethane 112°; m.p. of terpineolnitrolpiperidide 151 to 152°). The dihydroiodide melted at 77 to 78°.

718. Oil of Lovage Fruits.

- Lovage fruits yield upon distillation 0.8 to 1.1 p.c. of an oil that resembles that from the roots. $d_{15°}$ 0.935 to 0.936; $\alpha_D + 11°10'$ (one determination); $n_{D20°}$ 1.51308; A.V. 2.8; E.V. 125.2; soluble in 0.5 vol. of 90 p.c. alcohol, with 10 vol. of 80 p.c. alcohol it does not yield a clear solution.

[1]) F. A. Flückiger (*Pharmakognosie* III. ed., p. 460) found an oil, of which the origin is not mentioned, to be lævogyrate.

[2]) Comp. Report of Schimmel & Co. April 1909, 69.

[3]) Arch. der Pharm. 235 (1897), 2, 18.

[4]) Report of Schimmel & Co. April 1897, 27; October 1897, 11, footnote 3

719. Oil of Lovage Herb.

The fresh herb and flower stalks of lovage yield 0.05 to 0.15 p.c. of an oil which resembles that of the root as to odor.

$d_{15°}$ 0.904 to 0.945; $\alpha_{\wp}$ + 16 to + 46°; $n_{D20°}$ 1.484 to 1.487 (two determinations); A. V. 2.8 to 4.6 (two determinations); E.V. 152.6 to 152.7 (two determinations); soluble in 0.5 to 1 vol. of 90 p.c. alcohol and in 3 to 10 vol. of 80 p.c. alcohol with opalescence or the separation of floccules.

720. Oil of Angelica.

Oleum Angelicæ. — Angelikawurzelöl. — Essence d'Angélique.

Origin. Angelica, *Archangelica officinalis*, Hoffm. (*Angelica Archangelica*, L., Ger. *Engelwurz*), grows in places all over northern Europe as far as Siberia and is cultivated as a drug plant and for liqueur purposes. It is the most stately of the North European umbellifers and contains a peculiar aromatic oil in all parts, but more particularly in the root and in the fruit. The green parts of the plants are a favorite vegetable[1] in Norway, Sweden, Finland, Iceland and Greenland.

Production. The oils from both the root and fruit (angelica seed oil) find practical application. The fruits used for distillation come mostly from Thuringia and Saxony *(Erzgebirge)*, but occasionally those from France, Moravia and the Harz Mountains are also used in the production of oil.

The yield from the dry root amounts to 0.35 to 1 p.c.; from fresh roots, which yield a finer quality oil, 0.1 to 0.37 p.c.

Properties. When freshly distilled the root oil is an almost colorless liquid with a balsamic odor, which, exposed to air and light, becomes yellow to brownish in color. The odor is very aromatic, pepper-like with a suspicion of musk. The taste is spicy. $d_{15°}$ 0.859 to 0.918, the Thuringian oils frequently show a lower specific gravity, as low as 0.853[2]; α_D + 16 to + 41°; $n_{D20°}$ 1.477 to 1.488; A. V. to 3.8; E. V. 12 to 37; E. V. after

[1] Schübeler, *Die Pflanzenwelt Norwegens.* 1888. p. 280 and 303. — M. Rikli, Schweiz. Wochenschr. f. Chem. u. Pharm. 48 (1910), 48, 49, 65, 81, 97; Apotheker Ztg. 25 (1910), 157.

[2] Comp. Report of Schimmel & Co. October 1906, 10.

acetylation (seven determinations) 51 to 75, one distillate from Cölleda (Thuringia) root gave 35.5; soluble in 0.5 to 6 vol. and more of 90 p.c. alcohol, occasionally with slight turbidity.

Composition. Of an oil distilled by, F. Beilstein and Wiegand[1]) the bulk distilled over between 160 and 175°, a small portion between 175 and 200°, and even less above 200°. After repeated fractionations the lowest fraction had a constant boiling point of 158° and the composition $C_{10}H_{16}$. The terpene absorbed 1 mol. of hydrogen chloride, but yielded no solid hydrochloride. Fraction 170 to 175 , which constituted the bulk, likewise corresponded to the formula $C_{10}H_{16}$. After passing hydrogen chloride into this fraction a solid hydrochloride, melting at 127°, crystallized out. ·After repeated distillations over sodium that portion which boiled originally between 175 and 200° came over at the constant temperature of 176°. The analysis indicated a mixture of terpene and cymene. From the more difficultly volatile portion of the oil a hydrocarbon b. p. 250°, presumably a sesquiterpene, was isolated.

L. Naudin[2]) obtained upon fractionation a terpene, b. p. 166° with a pepper-like odor which he named *β*-terebangelene.

By means of its nitrite Schimmel & Co.[3]) proved the presence of *phellandrene.* Inasmuch as the chloroformic solution of this nitrite deviated the ray of polarized light to the left, and since the rotation of the nitrite is opposite to that of the underlying hydrocarbon, angelica root oil contains d-*phellandrene.*

The investigations of Beilstein, Wiegand and Naudin indicate that other terpenes, presumably pinene, are present. In all probability the *β*-terebangelene of Naudin is a mixture of phellandrene with a lower-boiling terpene. H. Haensel[4]), however, is of the opinion that phellandrene is the only terpene in angelica root oil.

The high-boiling fractions, which contain the bearer of the musk-like odor, have been examined by G. Ciamician and P. Silber[5]). From the last fraction of a steam-redistilled oil fine crystals separated upon standing which melted at 76 to 77°. The amount

[1]) Berl. Berichte 15 (1882), 1741.
[2]) Bull. Soc. chim. II. 39 (1883), 407. – Compt. rend. 96 (1883), 1153.
[3]) Report of Schimmel & Co. April 1891, 11.
[4]) Chem. Zentralbl. 1907, II. 1620.
[5]) Berl. Berichte 29 (1896), 1811.

was too small for a careful examination, but these crystals presumably represented the inner anhydride of a hydroxy acid. The oil distilled in vacuum was saponified with alcoholic potassa. The non-saponifiable portion had the characteristic odor of the sesquiterpenes and boiled between 240 and 270˚. From the saponification liquid sulphuric acid separated two acids: 1. a *valeric acid,* more particularly inactive methyl ethyl acetic acid, the potassium salt of which crystallizes with 5 molecules of water of crystallization; 2. *hydroxypentadecylic acid,* $C_{15}H_{30}O_3$, which, crystallized from ether, results in needles, grouped star-shape, that melt at 84˚. Of its derivatives the barium salt, the acetoxypentadecylic acid melting at 59˚, bromopentadecylic acid melting at 65˚, and finally the iodopentadecylic acid which crystallizes in pearly scales melting at 78 to 79˚, were prepared. It is noteworthy that the next lower homologue, the hydroxymyristic acid occurs in the oil of angelica fruit.

Likewise in one of the highest fractions E. Böcker and A. Hahn[1] found a lactone of the empirical formula $C_{15}H_{18}O_2$. From 200 g. of this "Nachlauf" 10 g. of lactone were obtained which, after recrystallization from ethyl ether and petroleum ether, melted at 83˚. It boils without decomposition, under 10 mm. pressure, above 250˚; $\alpha_D = 0˚$. It does not dissolve in either hot or cold caustic soda or potassa, however, it dissolves in hot alcoholic potassa. This compound is unsaturated. In glacial acetic acid it yields a dibromide which, recrystallized from glacial acetic acid, melts at 143 to 145˚ with decomposition. With hydrogen chloride it yields a hydrogen chloride melting at 101˚. Attempts to prepare the free hydroxyacid were unsuccessful. Judging from its stability and the tendency to reform from its hydroxyacid after saponification, the authors regard it as a γ-lactone.

The aqueous distillates resulting from this oil contain[2] *diacetyl* (m. p. of osazone 239 to 240˚), *methyl alcohol* (b. p. of benzoate 199 to 202°; d_{16}, 1.0894; E. V. 409, computed 412; m. p. of oxalate 54 to 55°), *ethyl alcohol* (b. p. of benzoate 213 to 213.5˚; d_{16}, 1.0576; E. V. 372.9, computed 373.9), *furfurol* (color reaction with aniline acetate), also a *base* having the odor of pyridine.

[1] Journ. f. prakt. Chem. II. 83 (1911), 243.
[2] Report of Schimmel & Co. April 1913, 26.

721. Angelica Seed Oil.

Yield. Angelica fruits yield upon distillation 0.7 to 1.5 p.c. of oil.

Properties. The oil from the fruits closely resembles that from the root; $d_{15°}$ 0.851 to 0.890; $\alpha_D + 11°$ to $+13° 30'$[1]); $n_{D20°}$ 1.486 to 1.489; A.V. up to 2.0; E.V. 13 to 30; soluble in 5 to 9 vol. of 90 p.c. alcohol, occasionally with opalescence and even turbidity, which may become very decided in individual cases.

Composition. Neither the investigations of R. Müller[2]), nor those of L. Naudin[3]), concerning the terpenes yielded positive results.

The only hydrocarbon proven to be present is *phellandrene*[4]). As in the case of the oil from the roots, phellandrene is probably not the only terpene present.

Of oxygenated constituents, Müller demonstrated the presence of two acids in the oil saponified with alcoholic potassa: 1. *Valeric acid,* which, as was demonstrated by the behavior of the barium salt, was methyl ethyl acetic acid. 2. *Hydroxymyristic acid* which crystallized in pearly scales melting at 51°. It occurs in the highest-boiling fractions and in the non-volatile residue. Several of its salts were prepared and analyzed, also the benzoyloxymyristic acid which crystallizes in small, white laminæ that melt at 68°.

722. Angelica Herb Oil.

The fresh angelica herb yields upon distillation 0.015 to 0.1 p.c. of oil[5]) which, as to odor, differs little or not at all from that of the roots. $d_{15°}$ 0.855 to 0.890; $\alpha_D + 8$ to $+ 28°$; $n_{D20°}$ 1.477 to 1.483; A.V. 3; E.V. 17 to 24; E.V. after acetylation 51.3 (one determination); soluble in 2.5 to 10 vol. of 90 p.c. alcohol, occasionally with slight opalescence[6]).

[1]) K. Irk (Kisérletügyi Közlemenyek 16 [1913], No. 5) has observed as high as $+ 14.62°$ in connection with Hungarian oil.

[2]) Berl. Berichte 14 (1881), 2476.

[3]) Bull. Soc. chim. II. 37 (1882), 107; Compt. rend. 93 (1881), 1146.

[4]) Report of Schimmel & Co. April 1891, 11.

[5]) *Ibidem* April 1895, 13.

[6]) Comp. Report of Schimmel & Co. April 1911. 20.

723. Japanese Angelica Oil.

Origin. In Japan two kinds of angelica are cultivated or account of their roots, *viz.*, *Angelica refracta*, Fr. Schmid: (Japanese *Senkiyu*) and *Angelica anomala*, Lall. = *Angelica japonica*, A. Gray (Japanese *Biyakushi*)[1]. From which of these the oil described below is derived is uncertain. Japanese angelica root[2]) is rather poor in oil, containing but 0.07 to 0.1 p.c.

Properties. $d_{15°}$ 0.905 to 0.908; α_D —1°40'; $n_{D20°}$ 1.49110; A.V. 10.6; E.V. 40. At 10° one of the two oils under examination separated crystals and at 0° congealed to a paste-like mass. The crystalline mass thus obtained by freezing and suction had the properties of a fatty acid which, after several recrystallizations, melted at 62 to 63° (impure hydroxypentadecylic acid?). The boiling temperature of the oil lay between 170 and 310°. The highest-boiling fractions were of a beautiful blue-green color. The residue congealed upon cooling and consisted for the most part of un-distilled acid.

The odor of the Japanese oil is very intense and persistent, more pungent than that of the German oil. Like the German oil it has an odor reminding of musk.

From the *fruits* of Japanese angelica, Murai obtained 0.67 p.c. of oil[3]).

724. Oil of Pseudocymopterus anisatus.

Upon distillation of *Pseudocymopterus anisatus,* Gray (C. et R.), which grows wild in the western United States, I. W. Brandel[4]) prepared a volatile oil the odor of which, like that of the fruits, is decidedly anise-like. Its specific gravity, 0.978 at 20°, corresponds closely with that of the oils of anise, star anise and fennel. However, it did not congeal at low temperature, a circumstance that is attributed to the presence of methyl chavicol.

[1]) J. J. Rein, *Japan*. Leipzig 1886. Vol. II, p. 159.
[2]) Bericht von Schimmel & Co. April 1889, 3; October 1889, 4; Report of Schimmel & Co. October 1907, 15.
[3]) Bericht von Schimmel & Co. October 1889, 4.
[4]) Pharm. Review 20 (1902), 218.

725. Oil of Asafetida.

Oleum Asæ Fœtidæ. — Asantöl, Öl von Asa fœtida. — Essence d'Ase Fétide.

Origin. Asafetida (Lat. *Asa fœtida*, Ger. *Asant, Stinkasant, Teufelsdreck*), is the inspissated milky juice of several species of *Ferula*. *Ferula alliacea*, Boiss., growing wild in northeastern and eastern Persia, yields the *hing*, the variety of asafetida used mostly in India, whereas the asafetida of European commerce, the *hingra*, is derived from *Ferula fœtida*, Regel (*F. Scorodosma*, Bentley et Trimen; *Scorodosma fœtidum*, Bunge), which grows in southern Turkestan, Persia, and Afghanistan[1]).

The asafetida which appears in the London and Hamburg drug markets is exported, for the most part, from Bender Abbas and Bushir, ports on the Persian Gulf[2]).

Production. Upon distillation with water vapor, asafetida yields 3 to 19.6 p.c. of volatile oil. High yields have been observed particularly by J. C. Umney and S. W. Bunker[3]), also E. F. Harrison and P. A. W. Self[4]).

Properties. Oil of asafetida is a colorless to yellow or brown liquid[5]) of a very unpleasant odor reminding of onions and garlic. In connection with a large number of oils distilled from Persian asafetida, Harrison and Self determined the following constants; $d_{15.5°}$ 0.915 to 0.993; $\alpha_D + 10°58'$ to $-17°3'$; $n_{D20°}$ 1.4942 to 1.5259; sulphur content 8.9 to 31.4 p.c.

A gum resin obtained from Bombay yielded 7.5 p.c. of an oil with somewhat different properties: $d_{15.5°}$ 0.993; $\alpha_D - 35°55'$; $n_{D20°}$ 1.5250; 37.8 p.c. sulphur. The sulphur content was determined according to the following method: —

About 0.5 g. of oil are transferred to a 150 ccm. flask provided with a condenser tube ground into the neck of the flask. Through this tube 5 ccm. of water and 5 ccm. of nitric acid ($d_{15.5°}$ 1.42) are added. If necessary the flask is heated

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[1]) G. Watt, The commercial products of India. London 1908, p. 534.

[2]) H. G. Greenish, Pharmaceutical Journ. 90 (1913), 729.

[3]) Chemist and Druggist 77 (1910), 205.—Perfum. Record 1 (1910), 165.

[4]) Pharmaceutical Journ. 88 (1912), 205; 89 (1912), 139; Chemist and Druggist 80 (1912), 269; 81 (1912), 202.

[5]) According to H. M. Sechler and M. Becker (Americ. Journ. Pharm. 84 [1912], 4) pure asafetida yields a colorless distillate, that adulterated with galbanum or ammoniacum a colored distillate.

slightly in order to start the reaction which then proceeds rather lively. Then 3 g. powdered potassium bromide are added through the condenser tube, the mixture boiled for 10 minutes, allowed to cool and finally 5 g. of sodium hydroxide are added having previously been dissolved in a little water. The mixture, now alkaline, is carefully evaporated to dryness in a platinum dish, heated to a red heat, the fused mass dissolved in water, the nitric and nitrous acids removed by evaporation with hydrochloric acid and the sulphate determined in the customary manner.

According to Harrison and Self the sulphur assay of the oil is best computed with reference to ash-free drug. Experiences thus far would indicate that the sulphur value of an unadulterated drug should not be less than 1.5 p.c.

Composition. According to the investigations of H. Hlasiwetz[1]) the oil is free of oxygen and nitrogen and contains *hexenyl sulphide*, $(C_6H_{11})_2S$, and *hexenyl disulphide*, $(C_6H_{11})_2S_2$.

Very different are the results obtained by F. W. Semmler[2]), who found a small oxygen content and sulphides very different in composition. From the lowest fraction he separated, after repeated distillation over metallic potassium, two terpenes: —

A hydrocarbon, presumably *pinene* ($d_{10°}$ 0.8602; $\alpha_D + 32°\,30'$) which yielded a liquid dibromide, $C_{10}H_{16}Br_2$, and only scarcely, a second terpene that yielded a solid tetrabromide, $C_{10}H_{16}Br_4$.

From the higher boiling fractions the following compounds were isolated: —

A *disulphide*, $C_7H_{14}S_2$, b. p. 83 to 84° (9 mm.); $d_{15°}$ 0.9721; $\alpha_D - 12°\,30'$. It constitutes about 45 p.c. of the oil.

A *disulphide*, $C_{11}H_{20}S_2$, b. p. 126 to 127° (9 mm.); $d_{14°}$ 1.0121; $\alpha_D - 18°\,30'$. It constitutes 20 p.c. of the oil and to it the oil owes its disagreeable odor.

A *substance* $(C_{10}H_{16}O)_n$, b. p. 133 to 145° (9 mm.); $d_{22°}$ 0.9639; $\alpha_D - 16°$. It constitutes 20 p.c. of the crude oil. Treated with sodium it yields cadinene, $C_{15}H_{24}$.

A *compound* $C_8H_{16}S_2$, b. p. 92 to 96° (9 mm.).

A *disulphide* $C_{10}H_{18}S_2$, b. p. 112 to 116° (pressure?).

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[1]) Liebig's Annalen 71 (1849), 23.
[2]) Arch. der Pharm. 229 (1891), 1. — Berl. Berichte 23 (1890), ·3530; 24 (1891), 78.

726. Galbanum Oil.

Origin. The gum resin known as galbanum is the air-dried evaporated milky juice that exudes spontaneously from the trunk and larger branches of *Ferula galbaniflua,* Boissier et Buhse, *Ferula rubricaulis,* Boissier (*Peucedanum rubricaule,* H. Baillon; *Peucedanum galbanifluum,* H. Baillon), and possibly *Ferula (Peucedanum) Schaïr,* Borszczow, umbelliferous trees that grow principally in Persia.

Production and Properties. The aromatic, not unpleasant odor of galbanum is due to the large amount of volatile oil which it contains. The yield, on distillation, varies between 10 and 22 p.c. according to the age of the drug.

Galbanum oil is yellowish, has a specific gravity of 0.905 to 0.955[1]) and deviates the plane of polarized light either to the right or left, α_j, up to $+20°$ and up to $-10°$. According to Hirschsohn[2]) Persian galbanum yields a dextrogyrate oil, galbanum from the Levant, on the other hand, a ·lævogyrate oil; $n_{D20°}$ 1.494 to 1.506.

Composition. An oil examined by P. Mössmer[3]), which distilled almost completely between 160 and 165° cannot be regarded as a normal oil since the distillation was conducted with water from a glass retort, a method that would yield the lower boiling portions, but not the more difficultly volatile higher boiling hydrocarbons.

The dextrogyrate hydrocarbon $C_{10}H_{16}$ boiling at 160 to 161° yielded a crystalline derivative that corresponded in every respect with the compound obtained from turpentine oil. Mössmer did not obtain terpin hydrate by treating it with nitric acid, whereas F. A. Flückiger[4]) was successful. The terpene of galbanum is, therefore, d-*pinene,* as is further established by the investigation of H. Thoms and B. Molle[5]) who obtained its hydrochloride melting at 125° and its nitrosochloride melting at 103°.

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[1]) E. F. Harrison and P. A. W. Self, Pharmaceutical Journ. 89 (1912), 141; Chemist and Druggist 81 (1912), 204.

[2]) Jahresb. d. Pharm. 1875, 113.

[3]) Liebig's Annalen 119 (1861), 257.

[4]) *Pharmakognosie.* III. ed. 1891, p. 65.

[5]) Berichte d. deutsch. pharm. Ges. 11 (1901), 90.

According to O. Wallach[1]), fraction 270 to 280° contains *cadinene*, $C_{15}H_{24}$, the presence of which was established by the preparation of the hydrochloride melting at 117 to 118°.

727. Oil of Sumbul.

Oleum Sumbull. — Moschuswurzelöl. — Sumbulwurzelöl. — Essence de Sumbul.

Sumbul is an East Indian name applied to the roots of several plants, *viz.*, to the roots of *Nardostachys Jatamansi,* D.C., as *Sumbul Hindi,* of *Valeriana celtica,* L., as *Sumbul Ekleti, Sumbul Ekelti, Sumbul Kumi* and *Sumbul italicus*[2]), also to the root of *Dorema Ammoniacum,* Don., as *Bombay Sumbul* or *Boi*[3]), which is used as an adulterant of genuine sumbul.

Ferula Sumbul, Hooker fil. (*Euryangium Sumbul,* Kauffmann) yields the genuine sumbul root which was first brought to Europe in 1835. Upon distillation it yields 0.2 to 1.37 p.c.[4]) of a viscid, dark-colored oil that possesses a musk-like odor; $d_{15°}$ 0.941 to 0.964; α_D −6°20′ (one determination[5])); A. V. 7.0 (one determination); S. V. 24 to 92; with 10 vol. of 80 p.c. alcohol it is not completely soluble, but it dissolves in one vol. or less of 90 p.c. alcohol.

Nothing is known about the constituents of sumbul oil.

728. Oil of Gum Ammoniac.

Origin. The bulk of the gum ammoniac that enters European commerce comes from Persia, where it is derived from the umbellifer *Dorema Ammoniacum,* Don., whereas *Ferula communis* var. *brevifolia,* Mariz yields the Moroccan drug and *F. marmarica,* Aschers. et Taub. that coming from Cyrenaica.

Production. Upon distillation with water vapor gum ammoniac yields but little volatile oil. Schimmel & Co.[6]) obtained 0.1 to 0.3 p.c. whereas E. F. Harrison and P. A. W. Self[7]), who carried out seven distillations, obtained from 0.08 to 0.2 p.c.

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[1]) Liebig's Annalen 238 (1887), 81.
[2]) Pharmaceutical Journ. I. 7 (1848), 546.
[3]) F. A. Flückiger and D. Hanbury, Pharmacographia. II. ed. 1879, p. 313.
[4]) Report of Schimmel & Co. October 1907, 91.
[5]) Report of Schimmel & Co. October 1907, 91. The statement as to its dextrorotation is due to a printer's error.
[6]) Bericht von Schimmel & Co. April 1890, 47.
[7]) Chemist and Druggist 81 (1912), 204; Pharmaceutical Journ. 89 (1912), 141.

Properties. The dark yellow oil has a strong odor of the drug, at the same time reminding of angelica. $d_{15°}$ 0.8875[1]) to 0.891; α_D + 1°37' (one determination[1])); $n_{D20°}$ 1.47250[1]) to 1.4808[2]); A. V. 3.7; E. V. 40.5; E. V. after acetylation 106.4; soluble in 0.5 vol. and more of 90 p.c. alcohol[1]): it distills for the most part between 250 and 290°, only a small part coming over between 155 and 170°[3]). The oil is free from sulphur.

729. Sagapenum Oil.

Sagapenum is a so-called gum which is derived from a Persian *Ferula* species, presumably from *Ferula Szovitsiana*, D. C. From it A. Tschirch and M. Hohenadel[4]) obtained 19.2 p.c. of a volatile oil that contained 9.7 p.c. of sulphur.

730. Oil of Peucedanum officinale.

From the dry roots of *Peucedanum officinale*, L.[5]) (family *Umbelliferæ*), Schimmel & Co.[6]) obtained 0.2 p.c. of a yellowish-brown oil with an intense and persistent but not pleasant odor that rather reminds of the odor of senega root. $d_{15°}$ 0.902; α_D + 29°4'; S. V. 62. Standing in the cold, a solid substance separated from the oil. Upon recrystallization from alcohol it was obtained in faintly yellow laminæ that melted at 100°.

731. Oil of the Fruit of Peucedanum grande.

The oil of the fruits of *Peucedanum grande*, C. B. Clarke has an unusually strong, spicy odor that reminds of that of *Daucus* oil[7]). $d_{15.5°}$ 0.9008; α_D + 36°. It distills over between 185 and 228° but leaves a rather considerable residue[8]).

[1]) Report of Schimmel & Co. April 1915, 7.

[2]) Chemist and Druggist 81 (1912), 204; Pharmaceutical Journ. 89 (1912), 141.

[3]) A. Tschirch and H. Luz, Arch. der Pharm. 233 (1895), 552.

[4]) *Ibidem* 233 (1895), 259.

[5]) The comminuted root of *P. araliaceum* (Hochst.) Benth. et Hook. reveals a strong floral odor due to a volatile oil. (Notizbl. bot. Gart. Berlin-Dahlem No. 48 [vol. V], p. 239).

[6]) Report of Schimmel & Co. April 1895, 75.

[7]) *Ibidem* April 1891, 64.

[8]) W. Dymock, C. J. H. Warden and D. Hooper, Pharmacographia Indica. Vol. II, p. 126.

732. Oil of Peucedanum Oreoselinum.

From the herb of *Peucedanum Oreoselinum*, Moench *(Athamanta Oreoselinum,* L., Ger. *Bergpetersilie),* G. Schnedermann and F. L. Winckler[1]) distilled a volatile oil with a strong, aromatic odor reminding of juniper. Specific gravity 0.843. It boiled at 163° and consisted, as shown by elementary analysis, almost entirely of terpenes. With hydrogen chloride a liquid monohydrochloride, $C_{10}H_{16}HCl$, resulted.

Which terpene or terpenes underlie this hydrochloride does not become apparent from the meagre data.

733. Oil of Peucedanum Ostruthium.

Distillation of the dried roots of *Peucedanum Ostruthium,* Koch *(Imperatoria Ostruthium,* L., Ger. *Meisterwurz)* yielded 0.2 to 0.8[2]), and up to 1.4 p.c.[3]) of oil. It had a strong odor reminding of angelica and a pungent aromatic taste; $d_{15°}$ 0.877[2]); $d_{20°}$ 0.8766[3]); α_{D} + 66.5°[3]); it boils between 170 and 190°[2]).

As yet nothing has been revealed concerning the composition of this oil[4]).

734. Oil of Dill.

Oleum Anethi. — Dillöl. — Essence d'Aneth.

Origin. Dill, *Anethum graveolens,* L. *(Peucedanum graveolens,* Benth. et Hook.) is an umbelliferous plant that is indigenous to the Caucasus and the Mediterranean countries. At the present time it is cultivated in many other countries, *e. g.* Bavaria, Thuringia, Galicia, Roumania and Holland.

Production. Distilled with water vapor the crushed fruits yield 2.5 to 4 p.c. of oil. In England the complete umbels are harvested for oil distillation when they are completely developed, but not quite mature, because the oil of the fresh, unripe fruits is preferred to that of the mature and dry seeds[5]). This explains the deviation in the properties of the English oils.

[1]) Liebig's Annalen 51 (1844), 336.

[2]) Bericht von Schimmel & Co. October 1887, 35.

[3]) H. Haensel, Pharm. Ztg. 48 (1903), 58.

[4]) H. Hirzel, Journ. f. prakt. Chem. I. 46 (1849), 292; Pharm. Zentralbl. 1849, 37. — Wagner, Journ. f. prakt. Chem. I. 62 (1854), 280.

[5]) Chemist and Druggist's Diary 1908, 235.

The dried exhausted fruits contain[1]) 14.5 to 15.6 p.c. protein and 15.5 to 18 p.c. fat.   They are used as cattle fodder.

Properties.   The oil is colorless at first but upon standing becomes yellow.   The odor reminds strongly of caraway oil, but differs from it by its specific dill aroma.   The taste is mild at first, but becomes sharp and burning. $d_{15°}$ 0.895 to 0.915, in exceptional cases as high as 0.917, and mostly above 0.900; $\alpha_D + 70$ to $+82°$; $n_{D20°}$ 1.484 to 1.490; carvone content, determined with sodium sulphite (see Vol. 1, p. 584) about 40 to 55, seldom as high as 60 p.c.; soluble in 4 to 9 vol. and more of 80 p.c. alcohol, in exceptional cases even in 1.5 to 2 vol.

An English oil[2]) had the following properties: $d_{15°}$ 0.906; $\alpha_D + 80°2'$; soluble in 6 and more volumes of 80 p.c. alcohol. It gave a decided phellandrene test.   In connection with two other English oils Schimmel & Co. observed the following properties: $d_{15°}$ 0.9073 and 0.9245; $\alpha_D + 81°51'$ and $+73°30'$; $n_{D20°}$ 1.48365 and 1.48681; soluble in 6 to 7 vol. of 80 p.c. alcohol; carvone content 38 and 32 p.c.; both oils gave decided tests for phellandrene.

Dill fruits from Cape Colony yielded a distillate corresponding to the normal oil; $d_{15°}$ 0.9117; $\alpha_D + 77°3'$; soluble in 6 to 6.5 vol. of 80 p.c. alcohol[3]).

Composition.   The principal constituent of dill oil is *carvone*[4]) of which it contains from 40 to 60 p.c.   Inasmuch as the dill carvone has the same angle of rotation as the carvone from caraway oil, both are to be regarded as identical in every respect[4]) [5]).

As to the terpenes of this oil, O. Wallach[6]) proved the presence of d-*limonene* in fraction 175 to 180° by preparing its tetrabromide melting at 104 to 105°.

While limonene constitutes the bulk of the terpenes of dill oil, other terpenes are present.   R. Nietzki[7]) isolated 10 p.c. of

[1]) Uhlitzsch, Die landwirtschaftlichen Versuchsstationen 42 (1893), 62.

[2]) Report of Schimmel & Co. April 1897, 15.

[3]) Perfum. Record 1 (1910), 290.

[4]) J. H. Gladstone, Journ. Chem. Soc. 25 (1872), 1 *et seq.*; Jahresb. f. Chem. 1872, 816.

[5]) A. Beyer, Arch. der Pharm. 221 (1883), 283.

[6]) Liebig's Annalen 227 (1885), 292.

[7]) Arch. der Pharm. 204 (1874), 317.

a hydrocarbon $C_{10}H_{16}$, b.p. 155 to 160°, which yielded terpin hydrate, but no crystalline hydrochloride. This oil may have been adulterated. In connection with an English oil, which presumably was distilled from the immature umbels, Schimmel & Co. report[1]) that sodium nitrite and glacial acetic acid afforded a decided phellandrene reaction. Repeating this test with unfractionated German oils, negative results were obtained. However, when the first fraction of German dill oil was used the presence of *phellandrene* was established by means of its nitrite. The Spanish oil which, however, is commonly distilled from the herb, yields the phellandrene test without fractionation as does the English[2]).

Dill apiol, b.p. 285°, which occurs in East Indian dill oil, is not contained in the German oil distilled from the fruit. In an attempt to ascertain the presence of this substance by means of fractional distillation, it was ascertained that this oil contains next to no substance boiling higher than carvone[1]). In the flask there remained a small residue that congealed to a brown mass. From its petroleum ether solution crystalline laminæ melting at 64° were abtained. Judging from its indifference toward sulphuric acid, it consisted of *paraffin*.

Adulteration. From Galicia Schimmel & Co.[3]) obtained an oil that was grossly adulterated with anethol or an oil containing anethol, presumably fennel oil.

735. Oil of Dill Herb.

Origin. The dill oil distilled in Spain is distilled from the herb, probably herb with immature fruit. The English oil, which, as already stated on p. 373, is distilled from immature umbels, occupies an intermediate position between the Spanish and the normal oil from the ripe fruits.

Properties. The oil of dill herb is colorless or greenish-blue[4]): $d_{15°}$ 0.906 to 0.933; $\alpha_D + 37$ to $+51°$; $n_{D20°}$ 1.494 to 1.497; soluble in 3 to 5 vol. of 90 p.c. alcohol; the carvone content is

[1]) Report of Schimmel & Co. April 1897, 15.
[2]) *Ibidem* October 1898, 19.
[3]) *Ibidem* April 1910, 47.
[4]) *Ibidem* November 1908, 49.

small, one oil yielding 16 p.c. by the hydroxylamine method[1]). The oil contains much phellandrene, yielding a decided nitrite test with sodium nitrite and glacial acetic acid without previous fractionation.

Composition.   As shown by Schimmel & Co.[1]), the bulk of the oil from the herb of the dill plant consists of phellandrene, more particularly of *α-phellandrene* (α_D + 88° 22'; $d_{15°}$ 0.8494; m. p. of nitrite 109 to 113°[2]). Of other terpenes the oil contains *terpinene* (m. p. of nitrite 155 to 156°; melting point of dihydrochloride 51 to 52°; m. p. of terpinene terpin 136 to 137°), also *limonene* or *dipentene* (m. p. of *cis*-terpin hydrate 116 to 117°). Of oxygenated constituents the following were found[2]): small amounts of *carvone* (m. p. of semicarbazone 161 to 162°; *dill apiol* (m. p. of dill*iso*apiol 44 to 45°; m. p. of dillapiolic acid 150 to 151°), also a substance that melted at 44 to 45° and presumably was *dillisoapiol*. The high boiling fractions contain a blue substance, and the distillation residue consisted of a mass that congealed upon cooling.   Purified by means of absolute alcohol it was of waxy consistency.

736. East Indian Dill Oil.

Origin.   The oil from East Indian and Japanese dill, *Anethum Sowa,* D.C. (*A. Sowa,* Roxb.) differs not only in its physical properties but also in its chemical composition from that of *Anethum graveolens,* L.[3]).

Properties.   The East Indian oil, yield 2 to 3 p.c., has a specific gravity of 0.948[4]) to 0.970[5]) at 15°, and an optical rotation of + 41° 30'[5]) to + 47° 30'[4]).

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[1]) Report of Schimmel & Co. April 1903, 30.

[2]) *Ibidem* 1908, 49.

[3]) Although F. A. Flückiger and D. Hanbury (Pharmacographia) do not regard East Indian dill as a separate species modern opinion tends to look upon the   n (also Japanese) dill as distinct, both because of its botanical differences   also because of the great difference in the volatile oil. Hence it has been named *Anethum Sowa,* D.C. (Comp. Umney, Pharmaceutical Journ. 61 (1898), 176 and Report of Schimmel & Co. October 1898, 10.)

[4]) J. C. Umney, Pharmaceutical Journ. III. 25 (1895), 977.

[5]) Report of Schimmel & Co. October 1891, 21.

In connection with Japanese oil, J. C. Umney observed $d_{15°}$ 0.964 and $\alpha_D + 50° 30'$.

Composition. During the distillation of the Indian fruits a substance separated which sank in water, a phenomenon that had never been observed in connection with ordinary dill oil[1]). According to the investigation of G. Ciamician and P. Silber[2]) this specifically heavy substance is the *dill apiol,* an isomer of the closely related apiol from parsley oil. For its constitution, properties and derivatives see Vol. I, p. 491.

737. Parsnip Oil.

Origin. Parsnip, *Pastinaca sativa,* L., is cultivated extensively as vegetable, but also grows wild practically all over Europe. All parts of the plant contain oil, which, however, is most abundant in the fruits.

OIL OF THE FRUITS.

Fresh umbels with fruits of the wild plant yield 0.4 to 0.6 p. c., dry fruits 1.5 to 3.6 p. c. of oil. The yield from fruits of the cultivated plants is about half as great.

Properties. $d_{15°}$ 0.869[3]) to 0.885; α_D inactive or slightly lævogyrate up to $-0° 30'$, in one instance $+0.13°$ was observed[3]); $n_{D20°}$ 1.428 to 1.435; A. V. 2 to 10; E. V. 218 to 270; E. V. after acetylation 260 to 296; soluble in 2 to 3 vol. of 80 p. c. alcohol.

Composition. The chemical composition of the oil seems to change with the degree of maturity of the fruits.

J. J. van Renesse[4]) found that the largest part of an oil distilled from mature fruits boiled between 244 and 245° and consisted of the *octyl ester* of *normal butyric acid.* The acid obtained from the fraction boiling below 244° yielded upon analysis of the silver salt figures which indicated a mixture of butyric acid and acids with a lower carbon content. Whether this is propionic acid, as assumed by van Renesse, or some other acid, remains to be seen.

[1]) Report of Schimmel & Co. October 1891, 21.

[2]) Berl. Berichte **29** (1896), 1799.

[3]) H. Haensel, Apotheker Ztg. **22** (1907), 275.

[4]) Liebig's Annalen **166** (1873), 82.

More complex was an oil obtained by H. Gutzeit[1]) from ripe and half-ripe fruits. It consisted essentially of three fractions: 58.6 p. c. of fraction 195 to 210°, 29.3 p. c. of fraction 233 to 240°, and 12.1 p. c. of fraction 240 to 270°. In the aqueous distillate Gutzeit found *ethyl alcohol*.

H. Haensel[2]) analyzed the barium salt of a fatty acid, the results of which analysis agreed well with the formula for *heptoic acid*. Schimmel & Co.[3]) obtained during the investigation of several kilograms of parsnip oil a mixture of fatty acids from which appreciable amounts of *caproic acid* ($d_{15°}$ 0.934; b. p. 204 to 206°; silver determination of silver salt) resulted upon fractional distillation.

OIL OF THE UMBELS.

Dried umbels, from which the fruits had been removed, yielded upon distillation 0.3 p. c. of oil[4]) which had a dark reddish-brown color and which had a very faint odor of oil of ambrette seeds. $d_{15°}$ 1.0168; α_D — 0° 50'; $n_{D20°}$ 1.50049; A. V. 4.2; E. V. 62.9; E. V. after acetylation 86.2; soluble in 6.5 vol. of 80 p. c. alcohol with separation of paraffin.

OIL OF THE ROOTS.

The fresh roots of *Pastinaca sativa*, L. yielded 0.35 p. c. of a light yellow oil[4]) the odor of which reminded somewhat of vetiver. $d_{15°}$ 1.0765; α_D — 0° 10'; $n_{D20°}$ 1.52502; A. V. 3,9; E. V. 12.6; E. V. after acetylation 33.7; not completely soluble in 10 vol. of 80 p. c. alcohol, soluble in 0.6 vol. and more of 90 p. c. alcohol.

OIL OF THE ENTIRE PLANT.

From an Italian parsnip oil which had been distilled from the entire plant with a yield of 0.1 p. c. Roure-Bertrand Fils[5]) record the following constants: $d_{15°}$ 0.8970; α_D + 0° 6'; A. V. 5.6; S. V. 228.9; E. V. after acetylation 251.1; soluble in 2 vol. and more of 80 p. c. alcohol, the addition of more alcohol causing the separation of a considerable amount of *paraffin*.

[1]) Liebig's Annalen 177 (1875), 372.

[2]) Apotheker Ztg. 22 (1907), 275.

[3]) Report of Schimmel & Co. November 1908, 94.

[4]) *Ibidem* October 1906, 52. — In place of "dry roots" it should read "fresh root".

[5]) Berichte von Roure-Bertrand Fils April 1912, 28.

738. Oil of Heracleum Sphondylium.

Origin and Production. The fruits of *Heracleum Sphondylium,* L., Ger. *Bärenklau,* which is distributed throughout Europe, yield 0.3 to 3 p.c. of oil. However, this great difference is due less to fluctuation in the oil content than to differences in the water content of the fruits.

Properties. The oil is a yellowish liquid, with a peculiar penetrating and persistent odor, a sharp taste and an acid reaction. $d_{15°}$ 0.871 to 0.880; α_{D} $+0°12'$ to $+1°6'$; $n_{\mathrm{D}20°}$ 1.426 to 1.433; A.V. 4 to 16; E.V. 214 to 276; E.V. after acetylation 276 to 302; soluble in 0,5 to 1.2 vol. and more of 80 p.c. alcohol, some oils are soluble even in 9 to 10 vol. of 70 p.c. alcohol[1]).

Composition. The oils distilled from the fruits of several *Heracleum* species have no practical value, it is true, nevertheless they are interesting scientifically in more than one respect. On the one hand, they contain the fatty acid esters of several alcohols of the methane series that are otherwise difficultly obtainable. On the other hand the predominating constituents of the oils distilled from fruits in various stages of maturity admit of phyto-physiological conclusions. It has been ascertained that not only the oil content, but the chemical composition of the oils depends on the degree of maturity of the fruits. In the oils distilled from half-ripe fruits are found compounds with lower carbon content which are wanting in the oils of mature fruits and which apparently disappear during the growth of the plant. Hence it is assumed that the substances with a lower carbon content are formed first and that they are utilized later in the synthesis of the compounds with more carbon atoms.

A *Heracleum* oil examined by Th. Zincke[2]) boiled between 190 and 270° and consisted for the most part of the *acetic* and *caproic esters* of *normal octyl alcohol.* The free alcohol which was present is presumably not a normal constituent of the oil, but a product of hydrolysis of the esters resulting during the distillation.

Somewhat more complicated were two oils distilled by W. Möslinger[3]) which boiled between 110 and 291°. They

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[1]) Comp. Report of Schimmel & Co. October 1906, 41.

[2]) Liebig's Annalen 152 (1869), 1.

[3]) Berl. Berichte 9 (1876), 998; Liebig's Annalen 185 (1877), 26.

contained the following compounds: 1. *Ethyl butyrate*. 2. A *hexyl* derivative, presumable the *acetate*. Of esters of octyl alcohol principally *octyl acetate* and *octyl caproate*, also some *octyl caprinate* and *octyl laurate* and possibly also the esters of the acids between caproic and lauric acids. In the aqueous distillate *methyl alcohol, ethyl alcohol* and *ammonia* were found.

OIL OF THE UMBELS WITHOUT FRUITS.

The dried umbels deprived of their fruits were distilled by Schimmel & Co.[1]) who obtained 0.08 p. c. The odor of the yellowish-brown oil is very different from that of the fruits. $d_{15°}$ 0.9273; α_D — 0°48′; $n_{D20°}$ 1.46031; A.V. 16.2; E.V. 148.6; E.V. after acetylation 195.9; soluble in 1.1 vol. of 80 p.c. alcohol, the addition of more solvent causing opalescence and a decided separation of paraffin.

739. Oil of Heracleum giganteum.

Origin and Production. The dry, ripe fruits of *Heracleum giganteum* hort. (*H. villosum,* Fisch.) yield, upon distillation, as much as 3.6 p.c. of oil.

Properties. Two oils examined by Schimmel & Co.[1])[2]) revealed the following constants: $d_{15°}$ 0.8722 and 0.8738; α_D + 1°14′ and + 1°0′; $n_{D20°}$ 1.42402 (one observation); A.V. 1.6 and 3.7; E.V. 288 and 281; E.V. after acetylation 314 and 311; soluble in 1 and in 1.2 vol. and more of 80 p.c. alcohol.

Composition. The oil examined by A. Franchimont and Th. Zincke[3]) was distilled from a foreign species of *Heracleum*, in all probability *H. giganteum*. Its principal constituents were *hexyl butyrate* and *octyl acetate*.

Upon distillation of not fully ripe fruits of *Heracleum giganteum* hort. H. Gutzeit[4]) obtained 0.56 p.c. of oil, from mature and partly dry fruits as much as 2 p.c. Upon fractionation it distilled over between 130 and 250°, fraction 130 to 170° containing *ethyl butyrate*.

[1]) Report of Schimmel & Co. October 1906, 41.
[2]) *Ibidem* October 1906, 41; April 1908, 57.
[3]) Liebig's Annalen 163 (1872), 193.
[4]) *Ibidem* 177 (1875), 344.

The aqueous distillate contained *ethyl* and *methyl alcohols*. In the oil of ripe fruits the methyl alcohol predominated, whereas in the oil of the unripe fruit the ethyl alcohol predominated.

740. Oil of Daucus Carota.

Origin. The *fruits* of the carrot, *Daucus Carota*, L., Ger. *Möhre,* yield, upon distillation from 0.8 to 1.6 p.c. of oil. From French fruits, however, only 0.5 p.c. were obtained[1]).

Properties. The oil is colorless or yellow with a pleasant odor reminding of carrots. $d_{15°}$ 0.870 to 0.9440[1]); α_D — 11 to — 37°; $n_{D20°}$ 1.482 to 1.491; A.V. 1 to 5; E.V. 17 to 52, E.V. after acetylation (2 determinations) 77.5 and 95.7.

Composition. M. Landsberg[2]) suspected the presence of pinene in the oil and of a substance $C_{10}H_{18}O$ in the portion boiling above 200°, without, however, being able to identify them. Later E. Richter[3]) identified the following compounds: free *butyric acid* (probably *iso*butyric acid) and *palmitic acid* and, in ester combination, *acetic* and possibly also *formic acids*. From fraction 150 to 160° of the lævogyrate portions of the saponified oil, Richter isolated a fraction 158 to 166° ($d_{11°}$ 0.8633; $\alpha_{D15°}$ — 8.45° in which he proved the presence of *pinene* by means of its nitroso-chloride and its benzylamide. In fraction 168 to 176° ($d_{14°}$ 0.8624; $\alpha_{D15°}$ — 5.85°) he found l-*limonene* (nitrosochloride; m.p. of nitrol-piperidide 103 to 106°). The high-boiling portions contained a crystalline substance $C_{15}H_{26}O_2$, which Richter calls *daucol* and which he regards as a diatomic sesquiterpene alcohol. This compound, purified by means of its xanthogenic ester, crystallizes in white needles with a silky lustre that melt at 115 to 116°; $[\alpha]_{D14°}$ — 17.15 to — 17.47°. Acetylation yielded but one acetyl group although the presence of two oxygen atoms would seem to indicate the presence of two hydroxy groups. Bromine did not add.

The carrot *root*[4]) yields, upon distillation, but 0.0114 p.c. of a colorless oil with a specific gravity of 0.8863 at 11.2°.

[1]) Report of Schimmel & Co. October 1907, 31.

[2]) Arch. der Pharm. 228 (1890), 85.

[3]) *Ibidem* 247 (1909), 391, 401. — Comp. also E. Deußen, Berl. Berichte 43 (1910), 523 and Report of Schimmel & Co. April 1910, 29.

[4]) Wackenroder, Magaz. d. Pharm. 33 (1831), 145.

741. Laserpitium Oil.

From the fruits of a species belonging to the umbelliferous genus *Laserpitium*, H. Haensel[1]) obtained 1.87 p.c. of a dark green oil the odor of which reminded of anise and caraway. $d_{20°} 0.9538$; A.V. 3.2; S.V. 15.5; S.V. after acetylation 28.5. The presence of *limonene, eugenol* or *dihydroeugenol methyl ether,* and a *paraffin* melting at 57 to 58° was established.

Family: PIROLACEÆ.

742. Oil of Monotropa Hypopitys.

The oil of *Monotropa Hypopitys,* L., family *Pirolaceæ,* which is frequently found in forests as parasite on roots was first distilled in 1857 by F. L. Winckler[2]). From the plants with almost fully developed flowers he distilled an oil that corresponded to wintergreen oil from *Gaultheria procumbens.* Later E. Bourquelot[3]) once more proved the identity of this oil with that of wintergreen. His investigations reveal that the oil does not occur in the plant as such but in the form of a glucoside which, in all probability, is identical with the gaultherin isolated by A. Schneegans and J. E. Gerock[4]) from the bark of *Betula lenta.* Acted upon by an enzyme contained in the plant, or by dilute sulphuric acid, this glucoside is hydrolyzed into methyl salicylate and sugar.

Family: ERICACEÆ.

743. Oil of Labrador Tea.
Oleum Ledi palustris. — Porschöl. — Essence de Ledon.

Origin and Production. All parts of *Ledum palustre* L., family *Ericaceæ,* Ger. *Sumpf-Porsch* or *Porst,* yield upon distillation from 0.3 to 2 p.c. of volatile oil, which mostly is so rich in

[1]) Chem. Zentrabl. 1906, II. 1496.

[2]) Neues Jahrb. d. Pharm. 7 (1857), 107; Vierteljahrsschrift f. prakt. Pharm. 6 (1857), 571; Jahresb. f. Chemie 1857, 520.

[3]) Journ. de Pharm. et Chim. V. 30 (1894) 435 and VI. 3 (1896), 577. — Compt. rend. 119 (1894), 802 and 122 (1896), 1002.

[4]) Arch. der Pharm. 232 (1894), 437.

stearoptene that it congeals to a solid mass at ordinary temperature. Sometimes, however, exposure of fractions to the temperature of a freezing mixture will not induce crystallization[1]). According to J. Trapp the reason for the variable yield, also for the differences in the composition of the oil is to be found in the the difference of the stage of development during which the parts of the plants were distilled. If a large yield with a high stearoptene content is desired, the twigs must be distilled shortly before, during, or immediately after the flowering period. E. Hjelt, however, could not find that the season or stage of development exercised a particular influence on the amount of volatile substances.

Properties. Labrador tea oil is a greenish or reddish, viscid liquid of a penetrating, narcotic odor and a pungent, unpleasant and persistent taste. $d_{15°}$ 0.93 to 0.96. The portions of the oil freed from ledum camphor boil between 180 and 250°.

Composition. The oil, prepared first by Rauchfuss[2]) in 1796, has since that time been examined by numerous investigators[3]). However, B. Rizza[4]) and E. Hjelt[5]) were the first to reveal the chemical nature of the ledum camphor.

This substance crystallizes from alcohol in beautiful, long needles that melt at 104 to 105°. It boils at 282 to 283° and, in alcoholic solution, is slightly dextrogyrate, $[\alpha]j + 7.98°$. Ledum camphor is a sesquiterpene hydrate, $C_{15}H_{26}O$, the hydroxy group of which is so labile that its alcoholic nature cannot be proven directly. Treated with benzoyl chloride or sulphuric acid ledene, a sesquiterpene $C_{15}H_{24}$ boiling at 255°, results. Potassium permanganate does not act on it, thus showing that ledum camphor

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[1]) Bericht von Schimmel & Co. October 1887, 35.

[2]) Trommsdorff's Journ. der Pharm. 3 (1796), 189.

[3]) Meissner, Berl. Jahrb. d. Pharm. 13, II. (1812), 180. — Grassmann, Rep. f. d. Pharm. 38 (1831), 53. — A. Buchner *ibidem* 57 und Neues Rep. f. d. Pharm. 5 (1856), 1. — E. Willigk, Wiener Academ. Berichte 9 (1852), 302. — A. Fröhde, Journ. f. prakt. Chem. 82 (1861), 181. — J. Trapp, Zeitschr. f. Chem. 5 (1869), 350; Berl. Berichte 8 (1875), 542; Pharm. Zeitschr. f. Russl. 34 (1895), 561 u. 661. — N. Ivanov, Pharm. Zeitschr. f. Russl. 5 (1876), 577. — E. Hjelt and U. Collan, Berl. Berichte 15 (1882), 2500. — B. Rizza, Berl. Berichte 16 (1883), 2311.

[4]) Zeitschr. der russ. phys.-chem. Ges. 19, I (1887), 319; Chem. Zentralbl. 1887, 1257.

[5]) Berl. Berichte 28 (1895), 3087.

is a tertiary alcohol[1]). According to K. Lomidse[2]) it contains no double linkage as is shown by its behavior toward bromine.

As shown by E. Sundvik, ledum camphor is a strong poison acting on the central nervous system.

The liquid portion of the oil is a ketone of the formula $C_{15}H_{24}O$[1]).

744. Oil of Alpine Rhododendron.

From the leaves and flowers of several species of *Rhododendron* (family *Ericaceæ*), Ger. *Alpenrose*, H. Haensel[3]) distilled 0.123 p.c. of a yellow oil with the pungent aromatic odor of the alpine Rhododendron. $d_{18°} 0.8620$; $a_{D18.5°}$ - - 4.33°. With sodium acid sulphite traces of an aldehyde could be separated. The oil freed from aldehyde had a S.V. of 20.5 and after acetylation 36.2. Fraction 150 to 160° yielded small amounts of a nitrosochloride melting at 102 to 103° which, however, reacted neither with piperidine nor benzylamine.

Distillation of the woody stems yielded 0.0097 p.c. of an oil which resembled that from the leaves and flowers as to odor and color.

745. Oil of Wintergreen.
Oleum Gaultheriæ. -- Wintergrünöl. — Essence de Gaultheria.

Origin. *Gaultheria procumbens*, L., one of the North American *Ericaceæ*, occurs from New England to Minnesota and to the south as far as Georgia and Alabama. On account of the peculiar, pleasant odor and taste that is developed during the chewing of the leaves it was used at an early period by the colonists. Thus, *e. g.* during the Revolutionary War, they were used as a substitute for Chinese tea[4]).

Production. The production of wintergreen oil has always been carried out in a rather primitive way, since the distillation

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[1]) Comp. also H. Wienhaus, Berl. Berichte 47 (1914) 322 and Report of Schimmel & Co. November 1908, 139, footnote.

[2]) Farmaz. J. 42 (1903), 1037; Chem. Ztg. Repert. 27 (1903), 284.

[3]) Chem. Zentralbl. 1906, II. 1495; 1907, I. 1332.

[4]) C. F. Rafinesque, Medical Flora of the United States of North America. 1828. Vol. I, p. 204.

of the fresh plant has been conducted on the spot by small farmers. The industry was started in the New England States [1]), but was later extended to the wooded mountainous regions of New York, New Jersey, Pennsylvania, Virginia and Maryland. As stills, old copper, whiskey stills of different sizes, mostly with a capacity of from 200 to 400 gals. are used [2]). Occasionally large boxes of firm oak planks, about 8 ft. in length, 4 ft. high, and 4 to 5 ft. wide are constructed. For the most part, however, whiskey barrels made of oak staves held together by iron rings are employed. The perforated bottom is made to fit tightly on a cast iron kettle which is filled with water for distillation. The upper end of the barrel is provided with a copper helmet connected with a spiral condenser contained in a large wooden vat.

The distillation is carried out only during a few months of the year. The body of the still is filled with the chopped plant thoroughly moistened with water. This chopped material is allowed to stand over night and next morning the fire is started. As a rule the distillation is completed in eight hours. About 90 p.c. of the oil passes over between the first 2 to 3 hours, the remaining 10 p.c. in the course of the next 3 to 4 hours.

The crude oil is colored red from the iron of the condenser. The distiller on a small scale sells the crude oil to wholesale druggists who purify the oil by rectification [3]).

Detailed accounts have appeared in an American journal [4]) concerning the production of wintergreen oil in Monroe County, Pa. About 60 stills are distributed over an area of 200 square miles. Some of these stills are permanent, others are itinerant, being removed as soon as the region is stripped of material. The harvest begins about the middle of April and ends with the change of weather in fall. Up to the middle of September the temperature is such that the material must be distilled at once. An experienced picker can harvest about 100 lbs. per day.

The leaves harvested in September, *i. e.* the new growth of the past summer, constitute the best material. The old

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[1]) Proceed. Americ. Pharm. Ass. 28 (1880), 269; 30 (1882), 184.
[2]) Americ. Journ. Pharm. 51 (1879), 439.
[3]) *Ibidem* 56 (1884), 264.
[4]) Americ. Perfumer 5 (1910), 192.

is a tertiary alcohol[1]). According to K. Lomidse[2]) it contains no double linkage as is shown by its behavior toward bromine.

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[3]) Chem. Zentralbl. 1906, II. 1495; 1907, I. 1332.

[4]) C. F. Rafinesque, Medical Flora of the United States of North America. 1828. Vol. I, p. 204.

Fig. 27. Distillation of Wintergreen Oil in Virginia.

rotation, enable the detection of most adulterants, more
cularly that with petroleum which has been observed frequently.
Admixture of oil of *Betula lenta* which so closely resembles
wintergreen oil, or of artificial methyl salicylate can be recognized
only by the lowering of the angle of rotation below $-0°25'$.

The details for testing this oil have been described under
oil of sweet birch in Vol. II, p. 321.

An English journal[1]) recommends the following color reaction
for the detection of artificial salicylate: — To 5 drops of the oil
to be tested contained in a test tube 5 drops of a 5 p.c. alcoholic
solution of vanillin and 1 ccm. alcohol are added. To the well
mixed solution 2 ccm. of concentrated sulphuric acid are added
and the solution again shaken. Pure gaultheria oil yields an
intensely deep red, pure betula oil a deep blood-red color, artificial
ester a yellow color. The author concludes that it is possible
thus to differentiate pure natural oil from such to which much
artificial methyl salicylate has been added. However, he does
not claim, and rightly so, that the test will yield practical results.

Schimmel & Co.[2]) repeated the test with oils distilled by
themselves and could verify the results in a general way. They
found, however, that in connection with betula oil the color, at
first, was much lighter than with gaultheria oil. In the course
of time both shades became equally darker, so that finally a
difference was scarcely noticeable. Artificial oil revealed the
yellow color mentioned above.

Composition. *Methyl salicylate,* the principal constituent of
wintergreen oil, was known to W. Procter[3]) and A. A. Ph. Cahours[4])
since the forties of the past century. Concerning the minor
constituents opinions differed greatly. It was the investigation of
F. B. Power and C. Kleber[5]) that cleared up the nature of the
non-methyl-salicylate constituents of both oil of wintergreen and
oil of birch. In order to avoid decomposition these chemists
did not saponify the oil as had previously been done but availed

[1]) Perfum. Record 5 (1914), 60.

[2]) Report of Schimmel & Co. April 1914, 98.

[3]) Americ. Journ. Pharm. 14 (1842), 211.—Liebig's Annalen 48 (1843), 66.

[4]) Annal. de Chim. et Phys. III. 10 (1844), 327.—Liebig's Annalen 48
(1843), 60; 52 (1844), 327.

[5]) Pharm. Rundschau (New York) 13 (1895), 228.

themselves of the property of the methyl salicylate to form a readily soluble potassium derivative. By means of this all of the methyl salicylate was removed from the oil by shaking its ethereal solution with 7.5 p.c. potassium hydroxide solution. Only 1.05 p.c. of the oil did not combine with the alkali and remained as a semi-solid mass at ordinary temperature. It consisted of the following compounds: 1. A paraffin C_nH_{2n+2} which, since it melted at 65.5°, must be regarded as *triacontane*, $C_{30}H_{62}$. 2. An *aldehyde or ketone*, which, when regenerated from its bisulphite addition product, has the odor of oenanthaldehyde and which, upon oxidation with potassium permanganate, yields an acid, the silver salt of which corresponds to the formula $C_6H_{11}O_2Ag$. 3. An *alcohol* $C_8H_{16}O$, b.p. 160 to 165°, that corresponds to the aldehyde or ketone already mentioned. 4. An *ester* $C_{14}H_{24}O_2$ boiling between 230 and 235° (135° under 25 mm. pressure). Upon saponification this yields the alcohol $C_8H_{16}O$ and the acid $C_6H_{10}O_2$ which results upon oxidation of the ketone. The alcohol as well as the ester possess the very penetrating, characteristic odor which differentiates wintergreen oil from artificial methyl salicylate.

746. Oil of Gaultheria punctata.

Origin and Production. *Gaultheria punctata*, Blume (*Gaultheria fragrantissima*, Wall., *G. fragrans*, D. Don., *Arbutus laurifolius*, Buch.-Ham.)[1]) is a well developed shrub which occurs in groups over wide areas of the higher Nilgiri regions, but also occurs frequently to the south in the Palni and Travancore Hills[2]). Furthermore this shrub is found in the highlands of the Dutch Indies, in Java as well as in Sumatra. Its Malay name is *Sari moedjari*. The oil is called *Gondapoera* oil[3]).

This oil, also known as Indian wintergreen oil, is distilled by the natives around Utakamand (Nilgiri) from the leaves by simple water distillation in primitive copper stills, such as are used in India for the production of grass oils. The output is

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[1]) J. C. Sawer, Odorographia, vol. II, p. 340. — Comp. also E. Kremers and M. James, Pharm. Review 16 (1898), 105.

[2]) Report of Schimmel & Co. October 1911, 96.

[3]) Bulletin No. 48 van het Koloniaal Museum te Haarlem, July 1911, p. 125.

very insignificant. For the most part the producers are distillers of eucalyptus oil, who also distill some wintergreen oil. An expansion of the industry, however, is possible, since the crude material may be had in abundance.

The yield attained by the natives is very small, due possibly to improper methods. The oil is sold for domestic use only, and the demand does not appear to be large. Whereas J. E. de Vrij obtained a yield of 1.15 p.c., a distillation in Buitenzorg[1]) yielded only 0.75 p.c. of oil.

Properties. In connection with an Indian distillate, Schimmel & Co.[2]) observed the following constants: — $d_{15°}$ 1.1877; α_D inactive; $n_{D20'}$ 1.53485; E.V. 364.8 $=$ 99 p.c. of methyl salicylate; soluble in 7 vol. of 70 p.c. alcohol. An oil distilled in Buitenzorg[1]) had the following properties: $d_{20°}$ 1.175; α_D inactive; S.V. 360.6 $=$ 97.9 p.c. methyl salicylate.

Composition. De Vrij[3]) who in 1859 distilled the oil from plants which he found in the extinct volcano Patoea, Java, ascertained that it consisted almost exclusively of *methyl salicylate.*

In 1879 H. Köhler[4]) re-examined the same oil distilled by de Vrij without, apparently, knowing about the statements as to the composition of the oil made by de Vrij in 1871. The optically inactive oil boiled between 221 and 222°. Upon saponification it yielded an amount of salicylic acid, m.p. 155 to 156°, corresponding to pure methyl salicylate.

In all probability the *Andromeda Leschenaultii* which grows abundantly in the Nilgiri Mountains of India, and in the leaves of which J. Broughton[5]) in 1867 found methyl salicylate, is identical with *G. punctata,* Bl.

747. Oil of Gaultheria leucocarpa.

Like the oil of *G. punctata* that from the leaves of *Gaultheria leucocarpa,* Blume, indigenous to Java, is known as

¹) Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 47.
²) Report of Schimmel & Co. October 1911, 96.
³) Pharmaceutical Journ. III. 2 (1871), 503.
⁴) Berl. Berichte 12 (1879), 246.
⁵) Pharmaceutical Journ. III. 2 (1871), 281.

Gondapoera oil in the country of its production. It is used as a remedy, also as perfume. Thus it is employed to perfume the garments of Indian princes[1]). In Sumatra the leaves are chewed as a kind of *Sirih*[2]).

According to J. E. de Vrij[3]) the fresh leaves yield upon distillation 0.012 p.c. of oil which consists principally of *methyl salicylate*. H. Köhler[4]) examined the same oil, which was optically inactive and boiled at 221 to 223', thus verifying de Vrij's results.

748. Erica Oil.

Schimmel & Co.[5]) examined an *Essence de Bruyère*[6]) obtained from Australia which probably was derived from a species of *Erica*. This oil with an agreeable, aromatic odor had a faint bluish-green color (traces of copper); $d_{15°}$ 0.8587; α_D $+2°44'$; soluble in 4.5 vol. and more of 90 p.c. alcohol.

Family: PRIMULACEÆ.

749. Primula Root Oil.

In addition to cyclamin, a saponin, the roots of *Primula veris*, L.[7]), family *Primulaceæ*, contain the glucosides primverin and primulaverin of which the first yields the so-called *primula camphor*[8]). It is obtained upon distillation of the roots and separates from the distillate either as handsome, lustrous six-sided laminæ or as a semisolid mass. Its odor is fennel or anise-like. Its taste is at first burning, then sweet, again fennel-like. It melts at 49° and boils over 200°.

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[1]) Bulletin No. 48 van het Koloniaal Museum te Haarlem, July 1911, p. 125.

[2]) *Sirih* is a preparation made of various aromatic herbs used for chewing and esteemed by the Malays.

[3]) Pharmaceutical Journ. III. 2 (1871), 503.

[4]) Berl. Berichte 12 (1879), 247.

[5]) Report of Schimmel & Co. April 1904, 97.

[6]) As to a Tonkin oil designated *Essence de Bruyère* see Oil of *Cathetus fasciculata* (family *Euphorbiaceæ*), p. 146.

[7]) According to the Index Kewensis *Primula veris*, L. = *P. elatior*, Hill., *P. vulgaris*, Huds., and *P. officinalis*, Jacq.

[8]) L. Mutschler, Liebig's Annalen 185 (1877), 222. — Comp. also Hünefeld, Journ. f. prakt. Chem. 7 (1836), 57 and 16 (1839), ·111.

Upon distillation of 300 kg. of roots H. Brunner[1]) obtained 170 g. of crude camphor. The rectified product boiled at 255 and had a specific gravity of 1.2155. Upon saponification the camphor did not yield salicylic acid, as claimed by Mutschler, but *m*-methoxy salicylic acid melting at 140°. Like the camphor itself, it yields an intensively violet color with ferric chloride. The molecule contains two methoxy groups, hence primula camphor may be regarded as the *methyl ester of* m-*methoxy salicylic acid.*

A. Goris and J. Ducher[2]) observed that when the fresh roots of *Primula officinalis,* Jacq. are rubbed between the fingers an anise-like odor results which results from enzyme action.

Later A. Goris and M. Mascré[3]) ascertained that the roots of *Primula officinalis,* Jack., Ger. *Schlüsselblume,* contain the glucosides primverin and primulaverin, also the enzyme primverase. Their investigations were then continued with C. Vishniac[4]). According to a special method, described by them in detail, 1 kg. of fresh root yielded an average of 1 g. =0.1 p.c. of a mixture of crude glucosides. From this 20 to 25 p.c. of primverin and 10 to 15 p.c. of primulaverin were isolated. The extraction must have been incomplete for the volatile oil yield of the roots is 0.08 p.c. corresponding to a 0.2 p.c. yield of glucosides.

The roots of *Primula Kewensis,* hort. yielded 0.2 p.c. of glucosides, computed with reference to the fresh herb, which were identical with those found in the species previously mentioned.

Primverin is a glucoside $C_{20}H_{28}O_{13}$ that crystallizes without water of crystallization and which melts at 203 to 204° on the *bloc Maquenne,* hence its melting point is 206°. $[\alpha]_D$ --- 71.53°. Upon hydrolysis one molecule of primverin yields two molecules of monoses and one molecule of p-*methyl ether of β-resorcylic acid methyl ester.* It was impossible to characterize the monoses which are contained in the primverin molecule as biose, which is hydrolyzed during the action of the acid on the glucoside. The

[1]) Schweiz. Wochenschr. f. Chem. u. Pharm. 42 (1904), 305.

[2]) Bull. Sciences pharmacol. 13 (1906), 536. Through Pharm. Ztg. 51 (1906), 1104 and Pharmaceutical Journ. 77 (1906), 627.

[3]) Compt. rend. 149 (1909), 947; Report of Schimmel & Co. April 1910, 161.

[4]) Berichte von Roure-Bertrand Fils October 1912, 3. — Bull. Sciences pharmacol. 14 (1912), 577.

biose can be obtained from the glucoside by the action of prim-verase. It is a new biose and has been named primvcrose. Of the two monoses named above, one is probably a pentose, the other a hexose.

The p-methyl ether of β-resorcylic acid methyl ester (4-methoxy salicylic acid methyl ester) is the principal constituent of the volatile oil of primula root. It melts at 49°. Its constitution was recognized by elementary analysis and saponification to the p-methyl ether of β-resorcylic acid (4-methoxy salicylic acid) melting at 158 to 159°. This acid had the same properties as the product described by F. Tiemann and A. Parrisius[1]. Further proof of its constitution was supplied by demethylating with the aid of hydrogen iodide and subsequent decarboxylation, thus producing resorcinol.

The hydrolysis of primverin by means of enzyme and by means of acid is shown by the following equation:

I. *Cleavage by means of enzyme:* —

$$C_6H_3 \overset{\diagup COOCH_3}{\underset{\diagdown OCH_3}{- O - C_{11}H_{19}O_9}} + H_2O = C_{11}H_{20}O_{10} \mid C_6H_3 \begin{matrix} COOCH_3 & [1] \\ - OH & [2] \\ OCH_3 & [3] \end{matrix}$$

Primverin   Primverose p-Methylether-β-resorcylic acid methyl ester

II. *Cleavage by means of acids:* —

Primverin $+ 2H_2O = C_6H_{12}O_6 + C_5H_{10}O_5 \mid$ p-Methylether-β-resorcylic acid
             Hexose   Pentose   methyl ester.
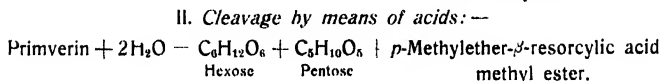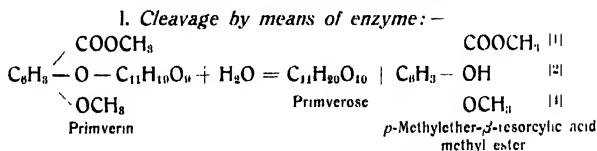
As primulaverin the authors designate a substance that melts at 161 to 163°; α_D —66.56°. It crystallizes with two molecules of water of crystallization and has the same empirical composition as primverin. It is probably a product of isomorphous crystallization of primverin with primulaverin proper, which has not yet been isolated in a pure state. The volatile oil which results upon hydrolysis of primulaverin is a mixture of the *methyl esters* of p-*methyl ether* of β-*resorcylic acid* and of m-*methoxy salicylic acid.*

In order to study the composition of the volatile oil of the root, 40 kg. of fresh primula root were well crushed and macerated with water during 24 to 28 hours. Upon distillation the mixture frothed considerably. From the aqueous distillate there separated

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[1] Berl. Berichte **13** (1880), 2376.

8.56 g. = 0.0214 p.c. of pearly scales, whereas the aqueous distillate contained in solution 26 g. — 0.065 p.c. of a mass about $^3/_4$ of which was solid. The total yield amounted to 0.0864 p.c. The solid mass crystallized from dilute alcohol in needles melting at 49 to 51°. When greatly diluted the solution has a decided odor of anise, in greater concentration its odor reminds of that of the cinnamates, later of that of salicylates of methyl and benzyl alcohols. Saponified, the solid mass yielded p-methyl ether of β-resorcylic acid (m.p. 158°); the liquid portions yielded principally m-methoxy salicylic acid (melting point 142 to 143°).

In order to obtain the oil of the *flowers* these were first covered with water and distilled after 6 hours' standing, yielding 0.00086 p.c. of a light green oil. The oil consists of saponifiable and non-saponifiable parts. The former likewise yielded the p-*methyl ether* of β-*resorcylic acid* and m-*methoxy salicylic acid*. The composition of the non-saponifiable portions has not yet been ascertained.

Whether primverase is a new enzyme has not yet been decided by the authors. Doubtlesly it is closely related to, if not identical with, betulase, which occurs in *Betula lenta, Gaultheria procumbens* and *Monotropa Hypopitys*. The enzyme was obtained as a powder from the dried leaves. The glucosides were first removed by extraction with alcohol and ether leaving the enzyme in the powdered leaves. Emulsin, invertin, the *Aspergillus* enzyme, and myrosin do not act on the primula glucosides. On the other hand the enzymes of *Monotropa Hypopitys, Betula lenta* and *Gaultheria procumbens*, when prepared like primverase, cause hydrolysis.

The question of the distribution of the enzyme in the Primula does not admit of definite answer. In the roots it predominates in the central cylinder. The overground portions contain it principally in the fibrovascular bundles or in the epidermal cells of the calyx and above all in those of the corolla. The glucoside is found in all parts of the plant.

Primverase is an enzyme very widely distributed in the family *Primulaceæ*. Its presence has been ascertained in *Primula elatior, P. Auricula*, L., *Samolus Valerandi*, L., *Lysimachia vulgaris*, L., *L. nemorum*, L., *L. nummularia*, L., *Anagallis arvensis*, L., *Hottonia palustris*, L., *Dodecatheon Meodia*, L., *Glaux mari-*

tima, L., and *Cyclamen latifolium*, Sibth. et Sm. Not always do the plants contain the glucosides as well as the enzyme.

Unlike *Primula officinalis*, not all fresh primula roots give off an anise odor when crushed in a mortar. However, the aqueous solution of the extracts yields the characteristic color reaction.

An *anise*-like odor is developed by: *Primula Kewensis*, Hort., *P. officinalis*, Jacq., *P. verticillata*, Forsk., *P. capitata*, Hook., *P. megaseifolia*, Boiss., *P. Poissonii*, Franck., *P. cashemiriana*, *P. rosea*, Boyle, *P. mollis*, Nutt. ex Hook., *P. Forsterii*, Stein. and *P. japonica*, A. Grey.

The odor of *methyl* or *amyl salicylate* is developed by: *Primula longiflora*, All., *P. frondosa*, Janka, *P. grandiflora*, Lam., *P. acaulis*, Hill., *P. cortusuoides*, L., *P. obconica*, Hance and *P. elatior*, Hill.

A *coriander*-like odor is developed by *Primula Auricula*, L., *P. pannonica*, A. Kern and *P. Palinuri*, Petagn.

In connection with *Primula involucrata*, Wall. no odor was observable.

Furthermore a faint odor of *methyl salicylate* was observed in connection with *Lysimachia nemorum*, L., whereas the roots of *Dodecatheon Meodia*, L. yield an *anise*-like odor upon crushing and *Anagallis arvensis*, L. a *valerian*-like odor.

The three last-mentioned plants likewise belong to the *Primulaceæ* family.

Family: OLEACEÆ.

750. Oil of Olive Leaves.

Dry leaves of *Olea europæa*, L. (family *Oleaceæ*) yield upon distillation 0.04 p.c. of a volatile oil of salve-like consistence, yellow color and a pleasant odor; m. p. 26.5°[1]).

751. Oil of Jasmine.

Origin and Production[2]). *Jasminum grandiflorum*, L. (family *Oleaceæ*) is a native of East India where it is used in the

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[1]) H. Haensel, Chem. Zentralbl. 1901, II. 419.

[2]) B. Marsh, Americ. Perfumer 2 (1907), 104. — L. Mazuyer, Journ. Parfum. et Savonn. 21 (1908), 194. — Ch. d'Aribenu, Parfum. moderne 6 (1913), 149.

production ·of perfume. On account of its fragrance the Spanish
jasmine has been cultivated in southern France for more than
150 years. In southern Europe the large flowering species is
grafted on the *Jasminum officinale*, L., which grows wild. In
March the wild plants are planted in rows 80 cm. apart, the
individual plants 10 cm. apart in the rows. In the following
year, or in the second year, the grafting is done and during the
summer of the same year the first flowers can be harvested.
The harvest begins toward the end of July and lasts until the
middle of October, the principal flowering season lasting from
the middle of August to the middle of ·September. In October
all of the plants must be covered with earth since they are very
sensitive to frost. One thousand plants yield between 25 and
65 kg. of flowers, or an average of about 40 kg. The hectare
with 100000 plants yields 4000 kg. of flowers. The annual con-
sumption of flowers in southern France is estimated between
4 to 6000000 kg. The principal centres of production are around
Grasse, Hyères and Seillans.

Although a volatile oil can be obtained by steam distillation
and subsequent extraction of the aqueous distillate with ether,
this method is not used in the technological production of the
perfume, neither is the method of extraction with hot fat or
vaseline. The most convenient method and the one requiring
least labor is the extraction with petroleum ether. However,
this does not afford as good a yield as does the enfleurage
process (See Vol. I, p. 288.) True, the yields according to this
method are not always nine times as great as those of the
extraction method as A. Hesse determined in connection with
his first experiments. Sometimes they are only again as great.
Nevertheless, the detailed investigations of Hesse[1]) show that
the flowers, after they have been cut, *i. e.*, under the conditions
under which the enfleurage process is conducted, produce con-
siderable amounts of perfume. Indeed, these investigations have
proven the correctness of Passy's hypothesis[2]).

[1]) A. Hesse and F. Müller, Berl. Berichte **32** (1899), 565, 765; A. Hesse,
ibidem **32** (1899), 2611; **33** (1900), 1585; **34** (1901), 291, 2916; **37** (1904), 1457. —
Chem. Industrie **25** (1902), 1.

[2]) J. Passy, Compt. rend. **124** (1897), 783. — Comp. vol. I, p. 246.
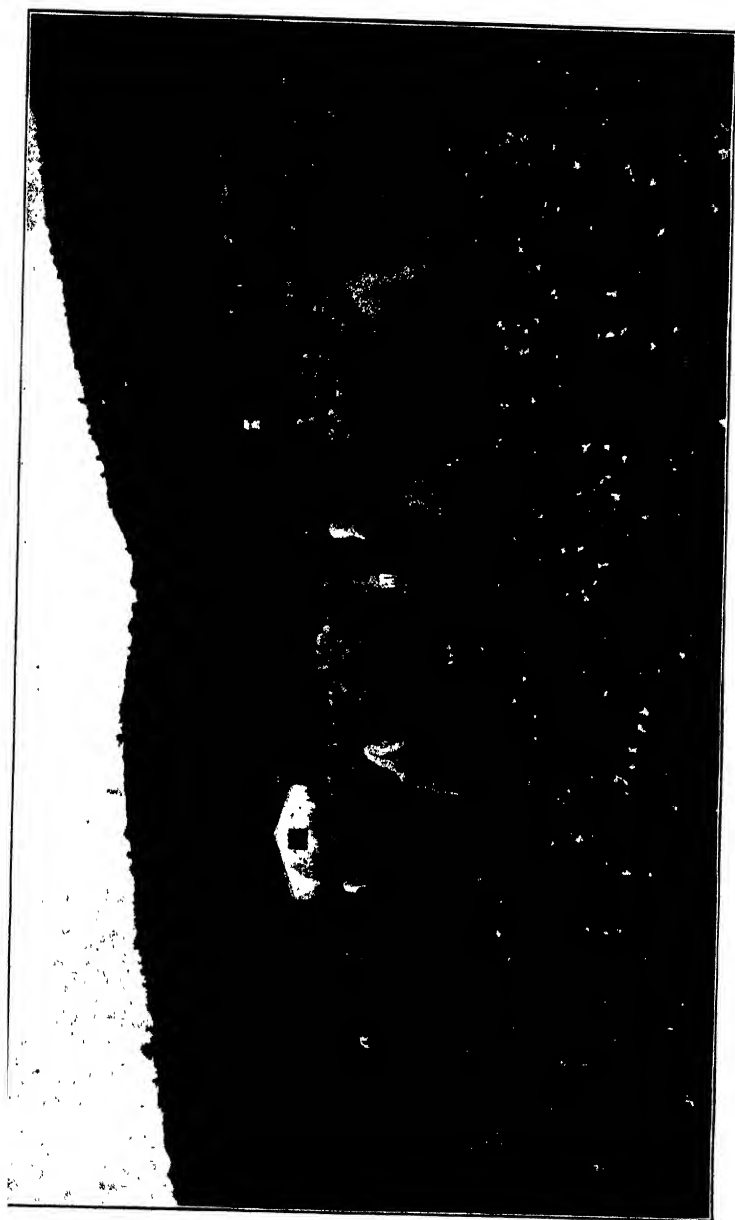
Fig. 28. Jasmin harvest in Seillans, Dép. du Var, southern France.

A jasmine pomade enters commerce from East India where it is likewise prepared by the enfleurage process, as described in 1839 in a letter by Dr. Jackson addressed to the publisher of *The Asiatic Journal,* of Calcutta[1]). Layers of sesamum seed are moistened with water. On top of these the natives place a layer of jasmine flowers, cover the whole with cloth and let stand for·12 to 18 hours. After that the fat, charged with perfume, is expressed from the seeds ground in an ordinary mill.

As already stated, the yield depends on the method of preparation. By means of the enfleurage process Hesse obtained 0.1784 p.c. of oil rectified by steam. From the flowers, after the enfleurage, steam distillation extracted an additional 0.0195 p.c. of oil. Computed with reference to the *enfleurage à froid* as made in France, the yield amounts to from 0.395 to 0.595 p.c. From Indian pomade Schimmel & Co. separated 0.3 to 0.4 p.c. of volatile oil of jasmine.

The yields obtained from extraction with petroleum ether vary considerably. In one instance Hesse obtained 0.0178 p.c., in another twice as much. H. v. Soden[2]), however, reports yields as high as 0.071 and 0.077 p.c. Upon distillation of fresh flowers with water vapor and extraction of the aqueous distillate with ether, Hesse obtained 0.0194 p.c. of jasmine oil.

Properties. The volatile oil of jasmine as such does not constitute an article of commerce, but is sold in the form of jasmine pomade or as concrete oil of jasmine (obtained by extraction). The properties of jasmine oil vary considerably[3]). In part this is due to differences in the method of preparation, in part to other causes. The specific gravity fluctuates between 0.920 and 1.015; the optical rotation between $-1°$ and $+4°15'$; the ester value between 155 and 270, which, computed as benzyl acetate, corresponds to an ester content of from 41 to 72 p.c.

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[1]) Watt, The commercial products of India.   London 1908, p. 820.

[2]) Journ. f. prakt. Chem. II. **69** (1904), 267.

[3]) The statements made by P. Jeancard and C. Satie (Bull. Soc. chim. **23** [1900], 556) about the properties of jasmin oil obtained by enfleurage with vaselin, are, according to Hesse (Berl. Berichte **34** [1901], 291) not exact, since the oil must have contained vaselin.

Composition. The first investigations on the composition of jasmine oil were published by A. Verley[1]) who claimed that the so-called "jasmol", the odoriferous principle of the oil, was the methylene acetal of phenylglycol. As was shown by A. Hesse and F. Müller[2]), this substance[3]) is not a constituent of jasmine oil. They in turn found considerable amounts of *benzyl acetate*[4]), also *benzyl alcohol* (benzaldehyde; m. p. of benzoic acid 121.5°), *linalool* (presumably dextrogyrate) and *linalyl acetate*. Later[5]), A. Hesse isolated other substances that are of greatest importance so far as the odor is concerned; *indol* (m. p. of picrate 52°), *anthranilic acid methyl ester* (m. p. of anthranilic acid 144 to 145°) and *jasmone*, a ketone of the formula $C_{11}H_{16}O$. This is a light yellow oil which becomes dark upon standing, has a specific gravity of 0.945 and boils at 257 to 258° under 775 mm. pressure. It is characterized by an oxime which crystallizes in fine needles that melt at 45° and by its semicarbazone that melts at 201 to 204°.

Hesse assigns the following quantitative composition to jasmin oil obtained by enfleurage:

65	p.c.	Benzyl acetate	2.5	p.c.	Indol
7.5	„	Linalyl acetate	0.5	„	Anthranilic acid
6	„	Benzyl alcohol			methyl ester
15.5	„	Linalool	3	„	Jasmone.

The occurrence of anthranilic acid methyl ester and of indol has not been observed in connection with all products. Thus

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[1]) Compt. rend. 128 (1899), 314; Bull. Soc. chim. III. 21 (1899), 226.

[2]) *Loc. cit.*

[3]) Schimmel & Co. (Report of Schimmel & Co. April 1898, 29) likewise, in their investigation made in 1895, found benzyl acetate and benzyl alcohol, also linalyl acetate, but no substance having the properties of jasmol.

[4]) In their patent application E. 5958 (D. R. P. 122290) H. and E. Erdmann mention a mixture of benzyl alcohol, benzyl acetate, linalool and anthranilic acid methylester as an illustration of artificial jasmin oil, without, however, stating that they had found these substances in genuine jasmin oil. On this statement they base a priority claim (Berl. Berichte 34 [1901], 2281) which Hesse (Berl. Berichte 34 [1901], 2916) contends together with other conclusions drawn therefrom. Comp. further: E. Erdmann, Berl. Berichte 35 (1902), 27.

[5]) *Loc. cit.*

some jasmin oils obtained by extraction with petroleum ether contained anthranilic acid methyl ester, others not. Again indol was found in some oils and not in others. As yet no explanation has been found for these peculiarities. It is possible that both indol and methyl anthranilate are contained in the flowers, not as such, but as condensation products which under conditions, as yet not understood, break up into their components[1]).

According to F. Elze[2]), p-*cresol* and *geraniol* are two other constituents of the oil of jasmin flowers. The p-cresol was isolated by means of 2 p.c. sodium hydroxide solution and characterized by converting it into p-cresol methyl ether (b.p. 175" under 748.5 mm.; d_{15° 0.964), which upon oxidation with potassium permanganate yielded anisic acid (m.p. 180°). In the oil deprived of p-cresol Elze proved the presence of geraniol in the fraction boiling between 75 and 102° (3 mm.). He isolated it by means of its calcium chloride compound after having treated the fraction previously with phthalic acid anhydride: b.p. 129 to 130° (25 mm.); d_{15° 0.883; α_D + 0°; m.p. of the diphenyl urethane 82°. The geraniol occurs in the oil in the free condition.

The wax which remains after the volatile oil has been washed out of the pomade has been examined by L. G. Radcliffe and J. Allan[3]) with the following results: — congealing point 56 to 57°; S.V. 65.8 (inasmuch as the wax was difficultly saponifiable, the operation had to be conducted in amyl alcohol solution); iodine value according to Wijs 52 to 53. Individual constituents were not identified in the wax.

Family: GENTIANACEÆ.

752. Oil of Menyanthes trifoliata.

From the dry herb of *Menyanthes trifoliata* L. (Ger. *Bitterklee* or *Fieberklee,* family *Gentianaceæ*), H. Hænsel[4]) obtained 0.0677 p.c. of a solid oil that melted at 37.5°.

[1]) Comp. von Soden, *loc. cit.*
[2]) Chem. Ztg. 34 (1910), 912.
[3]) Journ. Soc. Chem. Industry 28 (1909) 227.
[4]) Apotheker Ztg. 16 (1901), 281.

Family: APOCYNACEÆ.

753. Oil of Plumiera acutifolia.

Plumiera acutifolia Poir. (family *Apocynaceæ*) is a tree [1]) that is cultivated frequently in the cemeteries of the Philippines. From 40 kg. of the flowers, which have a faint odor reminding distinctly of frangipani, R. F. Bacon [2]) tried in vain to distill a volatile oil or even a floral water. Specially conducted experiments revealed that the fragrance is destroyed when heated to 40°. Extraction with low boiling petroleum ether and removal of the solvent by distillation in vacuum resulted in a gummy extract with a pleasant odor. Better results were obtained by maceration with paraffin oil.

754. Oil of Apocynum androsæmifolium.

The rhizome of *Apocynum androsæmifolium*, L., one of the North American *Apocynaceæ*, has been examined by C. W. Moore [3]). From the alcoholic extract water vapor drove over a small amount of volatile oil (3 g. from 19 kg. of rhizome = 0.016 p.c.) of light yellow color and a strong persistent odor: $d_{12°}^{12°}$ 0.948; b.p. 130 to 250°; $\alpha_D + 0°50'$. The oil gave a decided reaction for *furfurol*. The presence of *acetovanillone*, $CH_3O \cdot C_6H_3(OH) \cdot CO \cdot CH_3$ (m. p. 112 to 114°), was likewise established. Larger amounts of this substance were obtained from the non-volatile part of the extract, in part also as acetovanilloneglucoside, $CH_3 \cdot CO \cdot C_6H_3OCH_3 \cdot O \cdot C_6H_{11}O_5 + 2H_2O$, a new glucoside which Moore named *androsin*. It is readily soluble in hot dilute alcohol. Inasmuch as it is hydrolyzed by emulsin it is a β-glucoside.

755. Oil of Oleander Leaves.

The distillation of the leaves of *Nerium Oleander*, L. (family *Apocynaceæ*) yields 0.025 p.c. of a dark colored oil which at ordinary temperature is partly solid. It is slightly dextrogyrate and has a strong spicy odor and taste [4]).

[1]) A colored illustration of the flower is to be found in the Berichte von Roure-Bertrand Fils April 1909, 33. It is also pointed out there that the common designation *Plumeria* or *Plumieria* is not appliable.
[2]) Philippine Journ. of Sc. 4 (1909), A, 131.
[3]) Journ. Chem. Soc. 95 (1909), 734.
[4]) H. Haensel, Zeitschr. f. angew. Chem. 14 (1901), 989.

Family: ASCLEPIADACEÆ.

756. Oil of Chlorocodon Root.

The root of a *Chlorocodon* species (presumably *C. Whiteii*, Hooker f., family *Asclepiadaceæ*) having been sent from Uganda to the Imperial Institute in London, was examined by E. Goulding and R. G. Pelly[1]). It is know as *Murundo* by the natives and possesses an odor reminding of vanillin and piperonal. Upon distillation with water vapor it yielded 0.5 p. c. of a crystalline compound $C_7H_6O_2OCH_3$ which constitutes the fragrant constituent of the root and which proved to be a monomethyl ether of a dihydroxy benzaldehyde differing from vanillin. It melted at 41 to 42°, boiled at 257 to 258°, and was readily soluble in the ordinary solvents, but difficultly soluble in cold water. The oxime melted at 138°, the phenylhydrazone at 137 to 138°.

Later P. Friedländer[2]) established the identity of this compound with p-*methoxysalicylic aldehyde* prepared synthetically.

Schimmel & Co.[3]) report on a root, also obtained from Africa, which upon distillation with water vapor yielded 0.34 p. c. of oily distillate. In addition to small amounts of oil it consisted for the most part of the solid substance described above. Recrystallized from dilute alcohol it results in white, shiny needles that melt at 40 to 42°. The aqueous solution yields a reddish-brown color with ferric chloride. The entire oily distillate had a penetrating odor, reminding possibly of rhubarb, whereas the crystals, after several recrystallizations, had an odor of cumarin. Judging from these results it would seem that the root in question was chlorocodon root. The anatomical comparison of this root with a sample of the root examined by Goulding and Pelly, which was sent by the Imperial Institute in London, verified this surmise. However it could not be established with certainty that both roots belonged to the same species. Only two species of chlorocodon are known, *C. Whiteii*, Hook. f. and *C. ecornutum*, N. E. Br. The former occurs in

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[1]) Proceed. Chem. Soc. 24 (1908), 62; 27 (1911), 235.

[2]) Monatsh. f. Chem. 30 (1909), 879.

[3]) Report of Schimmel & Co. October 1911, 33.

Natal and South Africa, the latter in the Congo District and tropical East Africa.

The Imperial Biological-Agricultural Institute in Amani advised Schimmel & Co.[1]) that *Chlorocodon Whiteii*, Hook. f. occurs wild in German East Africa and is cultivated by the planters for its seed hairs. An experimental distillation in Amani of the fresh roots with water vapor yielded crystals which were compared with the crystals of Schimmel & Co. They were found to correspond. The rose-colored crude product melted at about 35° and after recrystallization from water, were obtained as white crystals. Dried in a sulphuric acid vacuum desiccator they melted at 43 to 45°. A mixture of both products showed no melting point depression.

Family: CONVOLVULACEÆ.

757. Oil of Rhodium.

Oleum Ligni Rhodii. — Rosenholzöl. — Essence de Bois de Rose[2]) ou de Rhodes.

The material that is quite generally said to be used in the production of oil of Rhodium, Ger. *Rosenholzöl*[3]), is the wood of the root of *Convolvulus scoparius*, L. and *Convolvulus floridus*, L. (family *Convolvulaceæ*) two shrubs growing in the Canary Islands.

The oil that now appears in the market as *Rosenholzöl* is mostly nothing more than either sandalwood oil or cedarwood oil to which rose oil has been added.

Oil of Rhodium has been examined by J. H. Gladstone[4]). Its origin can no longer be ascertained. It was viscid, had a density of 0.906 at 15.5° and an optical rotation of —16° in a 250 mm. tube. Four-fifths of the oil consisted of a hydrocarbon $C_{10}H_{16}$ (presumably $C_{15}H_{24}$) that boiled at 249° and had an odor of sandalwood and roses.

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[1]) Report of Schimmel & Co. April 1912, 42.

[2]) The wood designated *Bois de rose femelle* or *mâle* by the French is Cayenne or Guayana linaloe wood.

[3]) Comp. the investigations by R. Müller on the parent plant of rosewood. Pharm. Post 1903, 566; Pharm. Zentralh. 45 (1904), 41.

[4]) Journ. Chem. Soc. 17 (1864), 1 *et seq.*; Jahresb. f. Chemie 1863, 546, 549.

Of unknown botanical origin is likewise the oil distilled by Schimmel & Co.[1]) in 1887. This oil had a beautiful golden-yellow color, a pleasant rose-like odor and congealed at $+12°$ to needle-shaped crystals.

Material distilled some years later was derived from Teneriffe[2]). It corresponded partly to the description of the wood of the roots of *Convolvulus scoparius*, L. The odor of the oil did not come up to expectations. $d_{15°}$ 0.951; $\alpha_D + 1°30'$; S. V. 0; E. V. after acetylation 151.3. The oil yields slightly turbid solutions with 10 parts of 95 p.c. alcohol.

758. Oil of Jalap Root.

In their investigation of the constituents of *Exogonium purga*, Benth. *(Ipomœa purga,* Hayne, family *Convolvulaceæ)* F. B. Power and H. Rogerson[3]) distilled the alcoholic extract of the root drug with steam. Thus they obtained 0.0033 p.c. of a light yellow oil which upon standing soon became brown. It had an unpleasant, persistent, smoky odor. $d_{20°}^{20°}$ 0.8868; α_D inactive; boiling temperature 80 to 160° (60 mm.). With ferric chloride the dilute alcoholic solution gave a deep brownish-red color.

Family: VERBENACEÆ.

759. Oil of Lantana Camara.

Lantana Camara, L. is a widely distributed plant in Java[4]), New Caledonia[5]) and the Philippines[6]), as well as in British India and is cultivated in Europe as a houseplant. In the southern parts of British India it has become a veritable plague. Around Bombay ·it is known as *Ghaneri* and is popularly known as the heliotrope of the lowlands[7]). 1.000 kg. of leaves yield 250 g. of oil[8]).

¹) Bericht von Schimmel & Co. April 1887, 28.
²) Report of Schimmel & Co. April 1899, 37.
³) Journ. Americ. Chem. Soc. 32 (1910), 83.
⁴) Report of Schimmel & Co. October 1896, 73.
⁵) E. Heckel, Rev. cultures coloniales 8 (1901), 263.
⁶) Philippine Journ. of Sc. 4 (1909), A, 127.
⁷) Arch. der Pharm. 252 (1914), 1.

According to R. F. Bacon[1]) the yield seems to vary considerably according to age and season. 70 to 110 kg. of material afforded yields of from 60.245 to 78 cc. of oil. The oil is light yellow in color and has an odor reminding of sage. $d_4^{30°}$ 0.9132; $\alpha_{D30°}$ + 11.5°; $n_{D30°}$ 1.4913. Upon fractionation 50 g. of oil yielded 22 g. boiling between 125 and 130° (12 mm.) ($n_{D30°}$ 1.4892), and 24 g. boiling between 130 and 140° (41 mm.) ($n_{D30°}$ 1.4970).

An oil obtained from the Botanical Garden at Buitenzorg possessed different properties[2]): d_{15} 0.952; α_D — 0° 24′.

A sample sent by the Indian Institute of Science in Bangalore to Schimmel & Co.[3]) had been obtained from the flowers. It was a yellow liquid, the odor of which was but little characteristic; $d_{15°}$ 0.9274; α_D + 14°50′; A.V. 0.9; E.V. 24.3. On account of its large paraffin content its solution with even 95 p.c. alcohol did not remain clear. Upon the addition of more than 0.5 vol. of the solvent *paraffin* separated abundantly. Inasmuch as the sample was but a small one a more careful study was out of the question, even an acetylation. This, however, had been conducted in the Institute in Bangalore: $d_{26°}$ 0.915; $n_{D26°}$ 1.4987; S.V. 10; S.V. after acetylation 43.65.

The several parts of the plant growing in British India were distilled by D. D. Kanga[4]). The properties of the oil distilled from the fresh and dried flowers, also from the leaves are herewith tabulated: —

Oil from:	dried flowers	fresh flowers	leaves
Color	yellow	yellow	yellow
Odor	sage-like	likewise	likewise
Yield	0.07 p.c.	- - ·	0.2 p.c.
Density . . .	$d_{26°}$ 0.915	—	$d_{24°}^{24°}$ 0.9211
α_D	+ 23.9°	—	+ 1.96°
$n_{D26°}$	1.4987	1.5031	$n_{D27°}$ 1.48933
S.V.	10	—	—
S.V. after acetl.	43.6	—	—

[1]) Philippine Journ. of Sc. 4 (1909), A, 127.
[2]) Report of Schimmel & Co. October 1896, 73.
[3]) *Ibidem* October 1913, 66.
[4]) Arch. der Pharm. 252 (1914), 1.

760. Oil of Lantana odorata.

From the Department of Agriculture in Kingston, Schimmel & Co.[1]) obtained an oil distilled from the leaves of *Lantana odorata*, L. (family *Verbenaceæ*). This shrub grows in Jamaica and other islands of the West Indies. Its aromatic leaves are used as a tea in cases of cold, catarrh, indigestion, &c., also for aromatic baths and as a gargle. The yield 0.16 p.c. computed with reference to the leaves dried at 100°. The color was lemon-yellow, the odor hyssop-like, reminding at the same time of ambra. $d_{15°}$ 0.9149; α_D — 1° 36'; $n_{D20°}$ 1.49630; E. V. 4.7; E. V. after acetylation 51.0; soluble in 6 to 7 vol. and more of 90 p.c. alcohol. The bulk of the oil consists of constituents that boil above 200°.

761. Verbena Oil.

Origin and Production. Genuine verbena oil is distilled from the leaves of *Lippia citriodora*, H. B. et K. *(Verbena triphylla*, L'Hérit., *Aloysia citriodora*, Ort., family *Verbenaceæ)*, a plant that is cultivated for decorative purposes in Spain[2]), southern France and Central America. Inasmuch as its price is out of proportion to its value, the oil is not a regular article of commerce. For most purposes it can be replaced by the much cheaper lemon-grass oil, which for this very reason is known as East Indian verbena oil. Inasmuch as genuine verbena oil is but rarely to be had, statements concerning it must be taken with some reserve.

The fresh leaves yield 0.072[3]) to 0.195 p.c.[4]) of oil.

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[1]) Report of Schimmel & Co. November 1908, 140.

[2]) In order to ascertain the parent plant of "thyme lemon oil" J. C. Umney (Perfum. Record 3 [1912], 212) secured authentic distillation material from Spain and had it examined by E. M. Holmes who recognized it as *Thymus hyemalis*, Lange. This species is closely related with *T. hirtus*, Willd. and *T. vulgaris*, L. Boissier regarded it as *T. Mastichina*, L. and Pourret as a variety *(hyemalis)* of *T. sparsifolius*. It changes much in its appearance, nevertheless is readily distinguished from other species of *Thymus*. Umney's article contains illustrations of the entire plant, of the inflorescence and of parts of the flower.

[3]) E. Theulier, Bull. Soc. chim.-III. 27 (1902), 1113.

[4]) Berichte von Roure-Bertrand Fils April 1906, 38.

Origin	$d_{15°}$	α_D	$n_{D20°}$	Aldehyde resp. citral content
1. Grasse[1]	0.900	− 12° 38′	—	35 p.c.
2. ? [2]	0.902	− 12.7°	—	28 p.c.
3. Grasse[3]	0.919	−·16° 20′	—	20.8 p.c.
4. „ [4]		−·14° 16′	—	35.4 p.c.
5. „ [5]	—	—	—	65 to 70 p.c.
6. „ [6]	0.912	− 15°	··	37.5 p.c.
7. ? [6]	0.905	− 12°	—	26 p.c.
8. ? [6]	0.918	− 16°	·—	21 p.c.
9. Grasse[7]	0.905	12° 30′	—	26 p.c.
10. Spain[7]	0.928	+ 2° 45′	—	13 p.c.
11. „ [8] . . . . . (Thyme Lemon Oil)	0.901	+ 18° 30′	—	20 p.c.
12. Spain[9] . . . . . (Thyme Lemon Oil)	0.9085	+ 9° 45′	—	—
13. Spain[10]	0.9239	−·5°25′	1.49047	30 p.c.
14. Australia[11] . .	0.894	− 16°	··	74 p.c.
15. ? [12] . .	0.881	− 6°		—

As a rule verbena oil does not yield clear solutions with 70 and 80 p.c. alcohol. Of 90 p.c. alcohol 1 vol. is mostly required, but upon addition of more solvent turbidity results at times. Oils 11 to 13 were soluble in 1 to 2 vol. of 80 p.c. alcohol.

Composition. *Citral* (m. p. of β-naphthocinchoninic acid 195 to 197°)[1] is the characteristic constituent of the oil. According to P. Barbier[5] and F. Tiemann[13], also M. Kerschbaum[7] it occurs in two isomeric forms.

[1]) Gildemeister and Hoffmann, The Volatile Oils, 1st ed. 1900, p. 593.
[2]) Chemist and Druggist 50 (1897), 218.
[3]) E. Theulier, Bull. Soc. chim. III. 27 (1902), 1113.
[4]) Berichte von Roure-Bertrand Fils April 1906, 38.
[5]) P. Barbier, Bull. Soc. chim. III. 21 (1899), 635.
[6]) W. A. Wrenn, Perfum. Record 1 (1910), 283.
[7]) M. Kerschbaum, Berl. Berichte 33 (1900), 886, 887.
[8]) E. J. Parry and C. T. Bennett, Chemist and Druggist 69 (1906), 481.
[9]) Report of Schimmel & Co. April 1907, 101.
[10]) *Ibidem* October 1918, 105.
[11]) Probably from *Lippia citriodora*. J. C. Umney, Pharmaceutical Journ. 57 (1896), 257.
[12]) J. H. Gladstone, Journ. Chem. Soc. 17 (1864), 1 *et seq.*; Jahresb. f. Chem. 1863, 546 and 549.
[13]) Berl. Berichte 33 (1900), 884.

In a French oil E. Theulier[1]) found l-*limonene* (tetrabromide), *geraniol* (calcium chloride compound, oxidation to citral), a *sesquiterpene* and a hydrocarbon, presumably *paraffin*, melting at 62.5˙. According to Barbier[2]) the French oil contains *myrcene*.

From Spanish oil, M. Kerschbaum[3]) isolated 1 p.c. of a previously unknown ketone $C_{10}H_{16}O$, which he named *verbenone*: b. p. 103 to 104° under 16 mm. pressure; d_{17} 0.974; $\alpha_{D} + 66˙$; n_{D} 1.49951; m. p. of semicarbazone 208 to 209°; oxidation to norpinic acid melting at 173 to 174°.

It was likewise a Spanish oil (No. 13 of the preceeding table) that was examined by Schimmel & Co.[4]), who revealed the presence of a number of constituents some of which were new. 1) *Cineol* (m. p. of iodol compound 112 to 113°). 2) l-*Limonene* (m. p. of tetrabromide 103 to 104°). 3) *Citral*. 4) *Methylheptenone* (m. p. of semicarbazone 134 to 135´). 5) *Verbenone*, of which the oil contained scarcely 0.5 p.c. It could not be obtained in a pure state. The melting point of its semicarbazone could not be raised above 200 to 202°. 6) An *alcohol* having a characteristic odor reminding of citronellol and borneol, which may possibly be identical with the alcohol $C_{10}H_{18}O$[5]) found in cypress oil. 7) d-*Citronellol* (b. p. 224 to 230˙; m. p. of silver salt of acid phthalate 122 to 124°). 8) *Sesquiterpene derivatives* constituting 40 to 45 p.c. of the oil, *viz.*, a hydrocarbon, the constants of which (b. p. 256 to 264°; d_{15} 0.9121; $\alpha_{D} - 14° 42'$; n_{D20} 1.49431) would seem to indicate *caryophyllene*, and a *sesquiterpene alcohol* (b. p. 124 to 126° under 3 to 4 mm. pressure; d_{15} 0.9717; $\alpha_{D} - 7° 52'$; n_{D20} 1.50101) which yielded a liquid phenylurethane.

According to Roure-Bertrand Fils[6]) the roots contain 0.014 p.c. of volatile oil, the stems 0.007 p.c., and the inflorescences 0.132 p.c. The oil from the inflorescences showed an optical rotation $\alpha_{D} - 8° 24'$ and consisted of 29.6 p.c. of citral.

[1]) Bull. Soc. chim. III. **27** (1902), 1113.
[2]) *Ibidem* III. **21** (1899), 635.
[3]) Berl. Berichte **33** (1900), 886, 887.
[4]) Report of Schimmel & Co. October 1913, 105.
[5]) *Ibidem* April 1913, 51.
[6]) Berichte von Roure-Bertrand Fils April 1906, 38.

E. Charabot and G. Laloue[1]) have published an interesting paper on the formation and distribution of the volatile oil.

762. Oil of Lippia urticoides.

According to Th. Peckolt[2]) the fragrant flowers of *Lippia urticoides*, Steud. (family *Verbenaceæ*), a native of Brazil, yield 0.063 p.c. of volatile oil that has a neroli-like odor. $d_{28°}$ 0.908. The alcoholic solution shows a blue fluorescence (methyl anthranilate?).

763. Oil of Vitex trifolia.

The leaves of *Vitex trifolia*, L. (family *Verbenaceæ*) are used in India for baths, also as a remedy in various diseases. They contain a volatile oil that was distilled in the Botanical Garden in Buitenzorg[3]).

The odor of the oil is agreeably spicy, somewhat camphor-like. The latter characteristic is due to *cineol*, the presence of which was proven by means of the iodol test.

Other properties of the oil are[4]): $d_{27.5°}$ 0.884; α_{D} -39.75°. The aqueous distillate contained *methyl alcohol*.

764. Oil of Vitex Agnus-Castus.

The leaves of *Vitex Agnus-Castus*, L., Ger. *Keuschlamm* or *Abrahamsstrauch*, also *Mönchspfeffer*, were used by the ancient Greeks as aphrodisiac. Distilled by Schimmel & Co.[5]) they yielded 0.48 p.c. of volatile oil of a brown color and a not unpleasant, hyssop-like odor. It showed the following constants: $d_{15°}$ 0.9010; α_{D} -7°55'; A. V. 6.4; E. V. 18.3; E. V. after acetylation 58.4; soluble in 0.4 vol. and more of 90 p.c. alcohol. Under 4 mm. pressure it distilled between 31 and 120°. Of its constituents the presence of *cineol* was proven definitely. In addition it

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[1]) Berichte von Roure-Bertrand Fils October 1906, 10. — Bull. Soc. chim. IV. 1 (1907), 640. — Compt. rend. 144 (1907), 808.

[2]) Berichte d. deutsch. pharm. Ges. 14 (1904), 469.   The leaves of *Lippia geminata*, H. B. et Kth. contain 0.123 p. c., those of *L. microcephala*, Cham. 0.006 p.c. oil. *Ibidem* 470, 471.

[3]) Report of Schimmel & Co. October 1894, 73.

[4]) Verslag 's Lands Plantentuin te Buitenzorg 1895, 39.

[5]) Report of Schimmel & Co. April 1908, 121.

seems to contain sabinene and a quinone. The presence of the latter is indicated by the dark brown color of fraction 50 to 86° (4 mm.).

An oil distilled by H. Haensel[1]) with a yield of 0.36 p.c. had the following properties: $d_{20°}$ 0.8993; A. V. 5; E. V. 20.8; E. V. after acetylation 56.5. It contained *palmitic acid, pinene, cineol*, a *sesquiterpene* and probably a readily decomposable *sesquiterpene alcohol*.

From the seeds H. Haensel[2]) distilled 0.47 p.c. of a light brown oil with a decided spicy odor: $d_{15°}$ 0.8960; A. V. 7.41; E. V. 24.0; E. V. after acetylation 40.0.

Family: LABIATÆ.

765. Oil of Rosemary.

Oleum Rosmarini. — Rosmarinöl. — Essence de Romarin.

Origin. The rosemary shrub, *Rosmarinus officinalis*, L. belonging to the *Labiatæ* is distributed all over the Mediterranean territory.

Production. In commerce three kinds of rosemary oil are recognized, *viz.* the Italian, the French and the Spanish.

The Italian or, more correctly, Dalmatian oil is produced in the islands of Lissa, Lesina, Solta and Torcola, along the Dalmatian coast, in which the plant grows wild and covers large areas[3]). If necessary the wild growth is supplemented by planting.

Most of the oil is distilled in Lesina, Lissa coming next. The "rosemary forests" are property of the municipalities, which auction the privilege of oil production to the highest bidder. The utilization of the "forests" is regulated by law to the effect that a complete utilization is permitted only every third year. The two other years are partially closed seasons during which only little oil may be distilled. The plant (leaves and branches)

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[1]) Chem. Zentralbl. 1909, I. 1477.

[2]) *Ibidem* 1910, I. 1612.

[3]) Comp. also C. O. Cech, Dingler's Polytechn. Journal 229 (1878), 466 and Report of Schimmel & Co. October 1896, 66; April 1908, 66.

are cut in June, hence after the flowering period, which lasts from February until April, is long passed. After the branches

Fig. 29. Rosemary harvest in the island of Lesina (Dalmatia).

have been dried by exposure to the sun from 14 days to 4 weeks, the leaves are stripped or threshed. In the island of Lesina the rosemary bush grows only on the western half and does

not occur cast of Gelsa. The centers of production and com-
merce in this island are Brusje and Grabje. The people of
Brusje occasionally take their stills to Solta, and inhabitants of
Grabje go for the purpose of distillation to the Pellegrino pen-
insula (western point of Lesina) and the island of Torcola.
According to the older method distillation is conducted from
whiskey stills over direct fire. These stills have the advantage
that they can be mounted wherever rosemary grows so that
the material does not have to be carried far. Inasmuch as
good roads are wanting this is important.

More recently steam distilling apparatus with permanently
mounted boilers have been constructed both in Brusje and in
Grabje (fig. 30). They operate more satisfactory than itinerant
stills and the yield is about 30 p.c. higher. With a charge of
from 120 to 130 kg. leaves 1.5 to 2.5 kg. of oil are ob-
tained, namely 1.2 to 2 p.c. From Dalmatian rosemary leaves
Schimmel & Co.[1]) obtained 1.4 to 1.7 p.c.

In Lissa the principal harvest is conducted every fourth
year. The distillation is conducted over direct fire only. From
Cittavecchia, a port in Lesina, the oil is shipped in tin cans to
Triest and thence enters the world's commerce, frequently
adulterated with turpentine oil.

Statistics as to the production of Dalmatian rosemary oil
are not available. According to inquiries made on the spot,
the production in those years when a complete harvest is made,
amounts to 20000 kg. This estimate corresponds with a state-
previously made by Flückiger[2]).

It is stated that in 1901 about 12000 kg.[3]) of oil were
produced and in 1903 about 17000 kg.[4]).

French rosemary oil is said to possess a finer fragrance.
It is produced in the departments Hérault, Gard, Drôme, Bouches
du Rhône, Var, Alpes-Maritimes and Basses-Alpes. The two
departments named first yield the bulk of the oil. Here the
rosemary shrub attains a height of 2 m. and together with
Thymus vulgaris constitutes the underbrush of the mountain

[1]) E. Gildemeister and K. Stephan, Arch. der Pharm. 235 (1897), 586.

[2]) *Ibidem* 222 (1884), 476.

[3]) Chemist and Druggist 61 (1902), 220.

[4]) Report of Schimmel & Co. October 1904, 81.

slopes[1]). The distillation is conducted in itinerant stills, such as are described under Lavender Oil. From dry French rosemary leaves Schimmel & Co.[2]) obtained 2 p.c. of oil, from the flowers 1.4 p.c.

More recently Spanish oil has gained considerably in importance. Large quantities are now produced in the mountains of the provinces Granada and Murcia, also in the coast district of the province Seville. However, the oil produced along the coast shows an unfavorably low specific gravity and a poor solubility[3]). The *Tomillares*[4]) of the mountainous regions ar frequently rosemary heaths. At times they are covered by *Rosmarinus officinalis (Romèro)*, at times this plant is accompanied by other labiates, namely *Lavandula Spica,* D.C., or spike, and *Salvia lavandulifolia,* Vahl[5]). These are frequently distilled with the rosemary and this admixture explains the varying character of Spanish rosemary oil. The distillation, which lasts from April to October[6]), is conducted in stills, illustrated under Oil of Thyme, which are heated over direct fire. Both fresh and dry herb are distilled.

The amount of Spanish oil distilled annually is estimated at about 25000 kg.

English[6]) rosemary oil, small amounts of which are distilled in Mitcham, Market Deeping and Ampthill from cultivated plants, scarcely plays a role on the market.

Composition. The following substances have been found in rosemary oil: 1. *α-pinene,* 2. *camphene,* 3. *cineol,* 4. *camphor,* 5. *borneol.*

[1]) Arch. der Pharm. 222 (1884), 475.

[2]) Report of Schimmel & Co. October 1893, Table (supplement) p. 38.

[3]) Perfum. Record 3 (1912), 61.

[4]) *Tomillares* are rocky meadows on which woody labiates predominate. M. Rikli, *Botanische Reisestudien von der spanischen Mittelmeerküste.* Zürich 1907, p. 34.

[5]) M. Willkomm, *Grundzüge der Pflanzenverbreitung auf der iberischen Halbinsel.* Leipzig 1896, p. 156, 160 &c.

[6]) Comp. E. M. Holmes, Pharmaceutical Journ. III. 12 (1881), 238 and III. 20 (1890), 581. — J. C. Sawer, Odorographia, vol. I. p. 370. — H. J. Henderson, Pharmaceutical Journ. 79 (1907), 599, 695; 85 (1910), 541. — Perfum. Record 4 (1913), 366.

Inasmuch as the investigations have hitherto been directed to finding specific substances, a complete re-examination of the oil ought to lead to the discovery of other substances.

α-Pinene. According to G. Bruylants[1]) rosemary oil is supposed to contain 80 p.c. of a lævogyrate hydrocarbon $C_{10}H_{16}$ boiling between 157 and 160°. From the low specific gravity, *viz.,* 0.885, the lævorotation, as well as from the large amount of terpene, it becomes apparent that, undoubtedly, the oil was adulterated with French turpentine oil. Inasmuch as the frequent adulteration with turpentine oil made it desirable to ascertain whether pure rosemary oil contains pinene or not, E. Gildemeister and K. Stephan[2]) examined the lowest fractions of an oil distilled by themselves from Dalmatian rosemary leaves. After repeated fractionation they obtained a fraction boiling between 156 and 158° ($d_{15°}$ 0.867; $α_D + 2°\,30'$) which, when treated in glacial acetic acid solution with amyl nitrite and hydrochloric acid yielded a nitrosochloride which, in turn, yielded pinene nitrolbenzylamine melting at 122 to 123°. It thus became apparent that rosemary oil contains pinene, presumably a mixture of *d-* and *l-α*-pinene.

Camphene. Fraction 160 to 162° ($d_{15°}$ 0.875; $α_D - 0°\,45'$) was treated with glacial acetic acid-sulphuric acid. Upon saponification of the reaction product *iso*borneol, m. p. 211 to 212°, was obtained. When the benzene solution of the *iso*borneol was boiled with zinc chloride, camphene boiling at 159 to 160° and melting at about 50° was regenerated. Hence oil of rosemary contains a second terpene, *viz., camphene,* which, judging from the slight rotation of the fraction, is optically inactive.

A commercial oil of rosemary distilled in Dalmatia yielded like results. The presence of both pinene and camphene was established. The lowest fraction of 40 kg. of this oil boiling below 150° had an odor of acetaldehyde, decolorized fuchsine sulphurous acid and was partly soluble in water. The insoluble portion was hydrated with glacial acetic acid-sulphuric acid, the reaction product having a distinct odor of linalyl acetate. This

¹) Journ. de Pharm. et Chim. IV. **29** (1879), 508; Pharmaceutical Journ. III. **10** (1879), 327; Jahresb. d. Chem. 1879, 944.

²) Arch. der Pharm. **235** (1897), 586.

behavior indicates the presence of *olefinic terpenes*, such as are contained in oils of bay, hops, origanum, &c.[1])
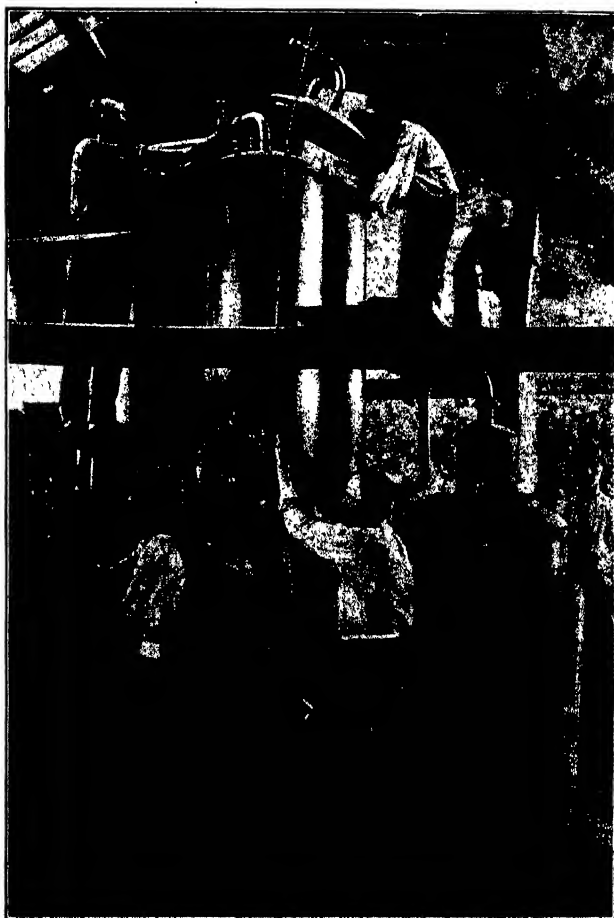
Fig. 30. Steam distillation apparatus for rosemary oil in the island of Lesina.

Cineol. In fraction 176 to 182° of rosemary oil E. Weber[2]) found cineol, $C_{10}H_{18}O$, which he isolated by means of its hydrogen

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[1]) Gildemeister and Stephan *loc. cit.*

[2]) Liebig's Annalen 238 (1887), 89.

chloride addition product. Identification was attempted by converting it into dipentene tetrabromide, $C_{10}H_{16}Br_4$, m. p. 123.5 to 124°; also into dipentene dihydriodide, $C_{10}H_{18}I_2$, m. p. 78.5 to 79°.

By passing hydrogen chloride into the ethereal solution of fraction 171 to 176°, Weber obtained dipentene dihydrochloride melting at 49 to 50°. This compound may result not only from cineol, but from any dipentene present. Inasmuch as the analysis of the fraction revealed the presence of much terpene, the formation of the hydrochloride is possibly due to dipentene (the terebene of Bruylants?).

Camphor and Borneol. The presence of camphor in rosemary oil was first observed by A. Lallemand[1]). Later J. de Montgolfier[2]) showed that rosemary camphor is a mixture of the dextrogyrate and lævogyrate modifications. Bruylants[3]) found that the stearoptene which crystallizes from the high boiling fraction of the oil consists not only of camphor, but also of borneol. In the oil, which, as previously stated, was grossly adulterated, Bruylants found 4 to 5 p. c. of borneol and 6 to 8 p.c. camphor. Hence pure oil must contain appreciably more of both substances. Gildemeister and Stephan[3]) determined the borneol content by acetylation and in two cases found 16.8 and 18.8 p.c. respectively. This assumes that rosemary oil contains no other alcohols, such as linalool and geraniol.

According to A. Haller[4]) camphor can be separated from borneol by heating the mixture with succinic acid whereby the borneol is converted into the acid succinate. According to Haller the borneol in rosemary oil, like the camphor, is a mixture of the optical isomers.

Judging from the saponification value, rosemary oil contains small amounts of esters, presumably of borneol. The acids thus combined have not yet been identified.

Properties. With regard to the specific gravity and optical rotation of commercial oils (Dalmatian, French and Spanish) the following general statements may be made. The specific gravity,

[1]) Liebig's Annalen 114 (1860), 197.
[2]) Bull. Soc. chim. II. 25 (1876), 117; Chem. Zentralbl. 1876, 102.
[3]) *Loc. cit.*
[4]) Compt. rend. 108 (1889), 1308.

for the most part, lies between 0.900 and 0.920, sometimes a little lower, but not below 0.894. The optical rotation is mostly dextrogyrate (up to $+$ 15°). However, lævorotation has been observed in connection with French and Spanish rosemary oils that were unquestionably pure (see below). Nevertheless, in most instances, lævorotation is due to adulteration with turpentine oil.

Upon fractionation of dextrogyrate oils in a Ladenburg flask, the first 10 p.c. also show dextrorotation as a rule, though occasionally the first 10 p.c. of unadulterated oils was lævogyrate. The cause for this peculiarity is not understood. A. Birckenstock[1]) believes that the season exercises an influence on the rotation of the oil. Thus he observed in connection with French oils that those distilled in spring were either lævogyrate or less strongly dextrogyrate than those distilled from plants from the same locality.

French distillates of A. Birckenstock	$d_{15°}$	α_D of the oil	α_D of the first 10 p.c.
Hérault, spring (April)	0.9121	$+$ 6° 32'	$-$ 4° 10'
Hérault, summer (July)	0.9115	$+$ 8° 17'	$-$ 0° 28'
Hérault, fall (End of November) .	0.9086	$+$ 11°	$+$ 1° 58'
Cannes, spring (13. April) . . .	0.9130	$-$ 0° 57'	$-$ 13° 38'
Cannes, summer (End of June) .	0.9118	$+$ 5° 57'	$-$ 2° 4'

However, generalizations are not permissible on the strength of these observations, for observations made in connection with Spanish material, yielded opposite results. Oils distilled in spring as well as in fall yielded first 10 p.c. fractions with higher angles than those of the original oil.

Spanish distillates of A. Birckenstock	$d_{15°}$	α_D of the oil	α_D of the first 10 p.c.
May	0.8851	$+$ 9° 47'	$+$ 14° 29'
October	0.9031	$+$ 3° 12'	$+$ 3° 30'

The English oils from cultivated rosemary seem to be mostly lævogyrate[2]). They are rarely dextrogyrate[3]), even though distilled in fall[4]).

[1]) Moniteur scientif. Quesneville, May 1906, 353; Journ. Parfum. et Savonn. 21 (1908), 231.

[2]) J. C Sawer, Odorographia, vol. l. p. 370.

[3]) H. J. Henderson, Pharmaceutical Journ. 79 (1907), 599, 695; 85 (1910), 541. — Perfum. Record. 4 (1913), 366.

[4]) Report of Schimmel & Co. October 1904, 82, footnote 1.

Even the Spanish oil which, as a rule, is strongly dextrogyrate, occasionally affords examples that are lævogyrate ($\alpha_D - 2°50'$) as shown by Schimmel & Co.[1])

Inasmuch as the properties of the three important commercial oils differ, they are herewith recorded separately.

DALMATIAN ROSEMARY OIL. $d_{15°}$ 0.894 to 0.912, for the most part not below 0.900; α_D dextrogyrate, $+0°43'$ to $+5°53'$; in only two out of more than 100 examinations higher values were found ($+7°20'$ and $+11°23'$), and in one instance only slight lævorotation was observed ($-1°$; α_D of the first 10 p.c. $\pm 0°$).

α_D of the first 10 p.c.[2]) dextrogyrate, at times higher, at times lower than the original rotation, in one instance only slightly lævogyrate ($-0°28'$).

$n_{D20°}$ 1.466 to 1.468; A.V. up to 0.7; E.V. 5 to 20 = 1.8 to 7 p.c. bornyl acetate; E.V. after acetylation 30 to 50 = 8.4 to 14.3 p.c. $C_{10}H_{18}O$. Mostly soluble in 80 p.c. alcohol (1 to 8 vol.). Of 90 p.c. alcohol 0.5 vol. or less suffice ordinarily. In individual cases up to 1 vol. is required.

FRENCH ROSEMARY OIL. $d_{15°}$ 0.900 to 0.920; α_D mostly dextrogyrate, up to $+13°10'$, in isolated cases also slightly lævogyrate; α_D of the first 10 p.c. ordinarily dextrogyrate, sometimes higher sometimes lower than the original rotation, rarely slightly lævogyrate; $n_{D20°}$ 1.467 to 1.472; A.V. up to 1.6; E.V. 3 to 14 = 1 to 4.9 p.c. bornyl acetate; E.V. after acetylation 29 to 42 = 8 to 11.3 p.c. $C_{10}H_{18}O$. The solubility is the same as that of Dalmatian oil.

SPANISH ROSEMARY OIL[1])[3])[4])[5]). $d_{15°}$ 0.900 to 0.920, but frequently somewhat below 0.9; $\alpha_D - 5°10'$ to $+11°30'$, mostly dextrogyrate; α_D of the first 10 p.c. at times dextrogyrate, at times lævogyrate. A.V. up to 1.5; E.V. 2.3 to 16.7 = 0.8 to 5.8 p.c. ester; E.V. after acetylation 35 to 50 = 9.8 to 14.3 p.c. alcohol $C_{10}H_{18}O$. The solubility is the same as that of the French oil.

[1]) Report o. Schimmel & Co. October 1910, 112.

[2]) For details see under Examination on p. 420.

[3]) A. Birckenstock, Moniteur scientifique de Quesneville, May 1906, 353.

[4]) P. Jeancard and C. Satie, Americ. Perfumer 6 (1911), 6.

[5]) E. I. Parry and C. T. Bennett, Chemist and Druggist 68 (1906), 671.

"ROSEMARY OIL COURANT" such as is occasionally offered in the trade is either a distillate of rosemary and of Spanish sage[1]) or of the latter alone. The constants of such oils are: $d_{15°}$ 0.9258 to 0.9356, $\alpha_D + 14$ to $+ 29°$, α_D of the first 10 p.c. $+ 0° 40'$ to $+ 12°$, $n_{D20°}$ 1,469 to 1.471, A.V. up to 1.0, E.V. 30.7 to 50.9 $=$ 10.7 to 17.8 p.c. ester, soluble in 0.7 to 2 vol. and more of 80 p.c. alcohol, individual oils are soluble in 70 p.c. alcohol (3 to 5 vol.).

Of less importance are the following oils: —

TUNESIAN ROSEMARY OIL[2])[3]). $d_{15°}$ 0.914 to 0.926; $\alpha_D - 0° 50'$ to $+ 3° 40'$; E.V. 4.8 to 8.4 $=$ 1.7 to 2.9 p.c. ester; E.V. after acetylation 43.4 to 53.2 $=$ 12.3 to 15.24 p.c. ester; soluble in 1 to 1.5 vol. and more of 80 p.c. alcohol.

ENGLISH ROSEMARY OIL[4]). $d_{15°}$ 0.901 to 0.924; $\alpha_D - 9° 35'$ to $+ 2° 32'$.

GREEK ROSEMARY OIL[5]) (2 oils). $d_{15°}$ 0.910 to 0.915; $\alpha_D + 1° 7'$ to $+ 1° 37'$; α_D of the first 10 p.c. $- 1° 30'$ to $- 4° 10'$; A.V. 0.5; E.V. 5.0; E.V. after acetylation 22 (A.V., E.V., E.V. after acetylation each 1 determination); soluble in 1 vol. and more of 80 p.c. alcohol.

CORSICAN ROSEMARY OIL[6]). $d_{15°}$ 0.9018; $\alpha_D + 17° 32'$; α_D of the first 10 p.c. $+ 15° 32'$; E.V. 36.0; E.V. after acetylation 83; soluble in 1 vol. and more of 90 p.c. alcohol.

SARDINIAN ROSEMARY OIL[6]). $d_{15°}$ 0.9028; $\alpha_D + 17° 20'$; α_D of the first 10 p.c. $+ 14°$; A.V. 1.0; E.V. 32.9; soluble in 10 vol. and more of 80 p.c. alcohol.

Examination. In testing rosemary oil special attention should be given to the specific gravity and angle of rotation which should correspond with the statements made under Properties. Turpentine oil, no matter from what source, lowers the specific gravity. Unless the amounts are insignificant, the presence of

[1]) Report of Schimmel & Co. October 1904, 82.

[2]) P. Jeancard and C. Satie, Americ. Perfumer 6 (1911), 6.

[3]) Report of Schimmel & Co. October 1905, 61.

[4]) R. A. Cripps, Pharmaceutical Journ. III. 21 (1891), 937. — Report of Schimmel & Co. October 1904, 82. — H. J. Henderson, Pharmaceutical Journ. 79 (1907), 599; 85 (1910), 541. — Perfum. Record 2 (1911), 141.

[5]) Report of Schimmel & Co. April 1910, 112.

[6]) Observation made in the laboratory of Schimmel & Co.

French turpentine oil causes a change in the angle to lævo-rotation. In order to detect the presence of small amounts which do not reduce the specific gravity to less than 0.9000 and do not reverse the angle of rotation[1]), 5 ccm. are fractionated from 50 ccm. oil in the Ladenburg flask described in vol. I, p. 566. The first 10 p.c. are then examined with the polariscope. So far as pure oils are concerned, this fraction will, as a rule, be dextro-gyrate. However, if but small amounts of French turpentine are present, the first 10 p.c. will be lævogyrate. (See also p. 417.)

Fractions of camphor oil are also frequently used as adulterant[1]). For the most part these change some one characteristic property of rosemary oil, either the angle of rotation (which is mostly increased) or the specific gravity or the solubility in 80 p.c. alcohol.

766. Oil of Prostanthera cineolifera.

The genus *Prostanthera*, family *Labiatæ*, comprises about 50 species, all of which are natives of Australia. The species *P. cineolifera* was first described by R. T. Baker and H. G. Smith[2]). The fresh herb yielded 0.71 p.c. of a yellowish oil which soon turned brown upon exposure to the air. $d_{15°}$ 0.9204; $n_{D20°}$ 1.4711. The oil deprived of phenols and aldehydes showed $\alpha_D + 4.1°$; S.V. 9.9; S.V. after acetylation 34.2. The S.V. of the acetylated oil, when saponification was effected in the cold, was 18.3. In the saponification liquid of the high-boiling portions of the non-acetylated oil *acetic acid* was found. Of phenols both *carvacrol* and *thymol* were found. In addition the oil contained *cuminic aldehyde* (m.p. of phenylhydrazone 126 to 127°), p-*cymene* (m.p. of p-hydroxy*iso*propyl benzoic acid 155°), *pinene* (?), and as principal constituent *cineol* (about 61 p.c., determined by means of the resorcinol method).

A sample sent by Baker and Smith was examined by Schimmel & Co. with the following results: It was a light brownish liquid, the odor of which resembled that of the oils of eucalyptus and cajuput. $d_{15°}$ 0.9477; $\alpha_D + 3°58'$; $n_{D20°}$ 1.47319; A.V. 2.7; E.V. 17.4; soluble in 1 vol. and more of 80 p.c. alcohol. The

[1]) Report of Schimmel & Co. April 1898, 69. – Comp. *ibidem* April 1905, 70, and Perfum. Record 4 (1913), 270.

[2]) Journ. and Proceed. Royal Soc. of N. S. W. 46 (1912), 103. — Report of Schimmel Co. October 1918, 89.

cineol content amounted to about 35 p.c. (resorcinol method), the phenol content about 2 p.c.

767. Oil of Lavender.

Oleum Lavandulæ. — Lavendelöl. — Essence de Lavande.

Origin. True lavender, *Lavandula vera*, D.C. (*L. officinalis* Chaix; *L. Spica* var. *α*, L.; *L. angustifolia*, Mnch.) occurs widely distributed throughout the Mediterranean region. In the Maritime Alps of southern France, more particularly at altitudes of from 700 to 800 meters it covers large areas and is there known as *lavande véritable* or as *lavande femelle*[1]). As pointed out by L. Lamothe in his brochure on lavender[2]), Jordan recognizes two sub-species of the true lavender, namely *Lavandula fragrans*[3]) *(lavande odorante, l. moyenne)* and *Lavandula delphinensis*, Jord. *(petite lavande, l. fine)*[4]) which yields the best oil. The former is widely distributed and occurs at the lower altitudes, whereas *L. delphinensis* occurs exclusively at the highest altitudes.

In addition there is a cross between *L. latifolia* (spike) and *L. fragrans*, which Reverchon[5]) designates *L. hybrida*, C. Chatenier *L. fragrans* × *latifolia* and Briquet[6]) *L. Burnati (grosse lavande, l. bâtarde, lavandin, spigoure)*.

According to Lamothe the distillers use the following designations for the several varieties: —

1. *Petite lavande.* This variety yields the best oil. It is more resistant and makes fewer demands than do the other two varieties that grow at lower altitudes.

2. *Lavande moyenne.* This yields a less fine quality, but nevertheless useful oil.

3. *Grosse lavande.* Bastard, yields an inferior oil. Not to be confounded with *grande lavande* (spike).

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[1]) The designation "femelle" as contrasted with "mâle" when applied to spike is used to indicate differences in size, not in sex characteristics.

[2]) *Lavande et Spic.* 2. ed. Le Grand-Serre (Drôme) 1908.

[3]) *L. fragrans*, Jord. is not mentioned in the Index Kewensis. *L. fragrans*, Salisb., however, is and is given as a synonym for *L. Spica*, Cav.

[4]) = *L. delphinensis* [Juss.], Briqu.?

[5]) According to the Index Kewensis *L. hybrida*, Reverchon and *L. delphinensis* are identical with *L. Spica*, Cav.

[6]) In Engler's *Pflanzenfamilien* (vol. IV, 3a, p. 228).

Production. The method of production which has long been in use in France is that of water distillation (figs. 33 to 36) which is adapted to the itinerant still, hence likewise used in the other countries. The still is charged with plant material and water and heated over direct fire. This method is convenient in so far as the stills can be carried from place to place wherever there are sufficient plants. Hence a distant transportation of plant material is avoided. This water distillation method, however, yields lavender oils with an ester content up to 40 p.c. only, for the distillation lasts very long so that the linalyl acetate is exposed during all this time to the saponifying action of the boiling water. If, however, steam distillation be employed *i.e.* if the stills filled with flowers are distilled with steam that has been generated in a separate boiler, as rapidly as possible, there results not only a larger yield, but the oil itself is more valuable containing as much as 50 to 55 p.c. ester and even up to 60 p.c.

Schimmel & Co. were the first to recognize the fundamental difference in the two methods of distillation and in 1905 erected a factory in Barrême (Départment Basses-Alpes) in which lavender oil is distilled by means of steam (see illustration p. 425).

The influence which the method of distillation exerts in the preservation of the esters has been ascertained experimentally by Schimmel & Co.[1]) The ester content of oils proved very different for those distilled by the steam method and those distilled by the water method, as practiced in southern France, from the same material. In the latter instance 50 to 60 kg. of flowers were covered with a like amount of water — for dry flowers somewhat more was taken — and the oil distilled in the ordinary manner from one of the usual stills. 16 L. of distillate were collected and the following results recorded: —

		Oil yield p.c.	$d_{15°}$	α_D	p.c. ester	Solubility in 70 p.c. alcohol.
1.	Steam distillation	0.81	0.8894	—8°4′	50.9	Soluble in 6 to 7 vol. and more with slight opalescence.
	Water distillation	0.71	0.8871	— 6°47′	44.0	Soluble in 3 vol. and more.
2.	Steam distillation	0.82	0.8905	---8°	53.7	Soluble in abt. 7 vol. and more with slight turbidity.
	Water distillation	0.75	0.8880	—6°21′	43.6	Soluble in 3.3 vol. and more.

[1]) Report of Schimmel & Co. April 1907, 63.

Fig. 31.   Itinerant still for lavender of Schimmel & Co. in Castellane (Basses-Alpes).

The loss in ester when the old method is used as compared with the results obtained according to the steam distillation method is appreciable. In one instance it amounted to 7 p.c., in another even to 10 p.c. Moreover, the steam distillation method affords a somewhat larger yield.

If the above data prove sufficiently the advantages of the steam distillation method, the *rapidity* with which *the distillation is conducted* is likewise of importance so far as the preservation of the esters is concerned as was demonstrated by numerous experiments. The faster the distillation is conducted, the higher the linalyl acetate content. Corresponding to the rapidity of the distillation oils with a 4 p.c. increase in ester content were obtained from the same plant material.

From fresh flowers a yield of 0.8 p.c. is obtained, from dry flowers up to 1.5 p.c. During drying the flowers suffer a considerable loss in weight which varies from 35 to 47 p.c. according to the length of drying period. Not only is moisture lost, but a part of the oil as well, as can be seen by computing the oil yield with reference to the fresh material. Inasmuch as the oil from dry material has a higher density and a higher ester content, it becomes apparent that, in the process of drying, the flowers suffer a loss principally of the more volatile constituents of the oil, the terpenes. The data contained in the following table may serve as commentary in this regard.

Material used	Loss upon drying	Yield of oil computed with refer. to fresh flowers	$d_{15°}$	n_D	p.c. ester	Solubility in 70 p.c. alcohol
1. a) Fresh flowers .		0.84 p.c.	0.8891	$-7°20'$	50.3	Soluble in 6 vol. and more with slight turbidity. Opalescence rem. after addition of 10 vol.
b) The same after drying $1^1/2$ days	35 p.c.	0.79 p.c.	0.8905	$-7°33'$	51.8	
2. a) Fresh flowers .		0.87 p.c.	0.8859	$-9°4'$	46.9	Soluble in abt. 4.5 vol. a. more, with opalescence.
b) The same after drying 4 days .	47 p.c.	0.79 p.c.	0.8884	$-9°33'$	49.2	
3. a) Fresh flowers .		0.80 p.c.	0.8875	$-8°10'$	47.1	Sol. in 3 vol. a m.
b) The same after drying 5 days .	47 p.c.	0,72 p.c.	0.8899	$-8°44'$	51.1	Sol. in 4.2 vol. a. m.

Small losses in the ester content naturally take place during the drying of the lavender flowers. However, they are small and amount to but 10 to 25 p.c. of the total oil loss.

From what has been said about the distillation of lavender, it follows *that the largest yields of oils with the highest ester content*
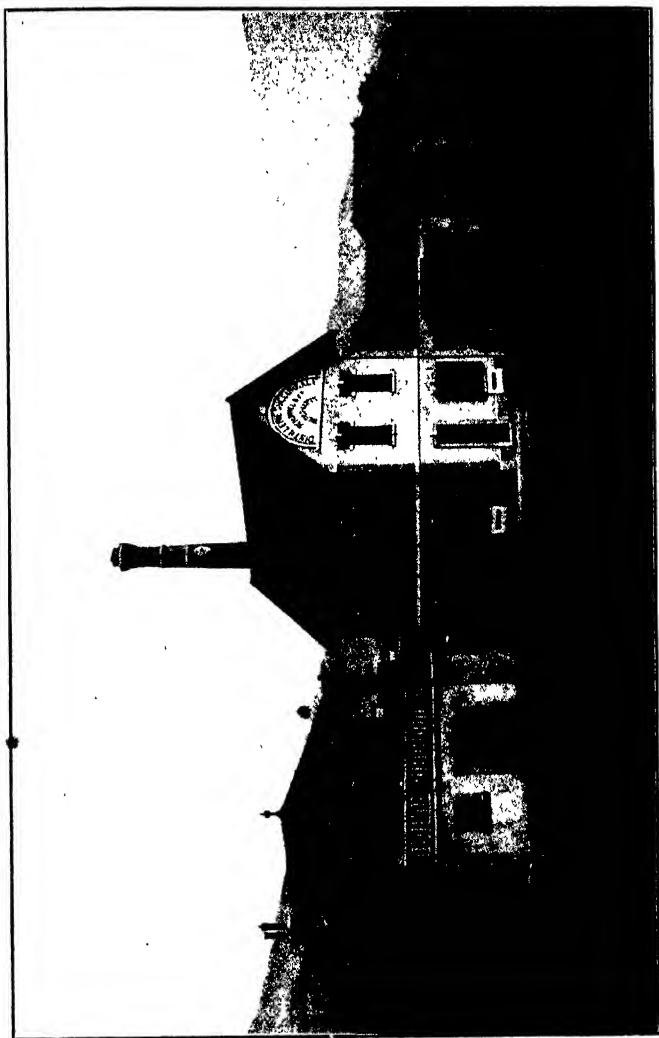
Fig. 32. Lavender oil factory of Schimmel & Co. in Barrême after its enlargement in 1912.

are obtained when lavender flowers are distilled very fresh and when the steam distillation is conducted as rapidly as possible.

The distillation is conducted during that period when the flowers are in full bloom, namely, from early July to early September. To distill later is not advisable, as a rule, since the quality of the oil decreases. Inasmuch as the inflorescences also lose flowers, the yield likewise diminishes.

The blossoms are not the only part of the plant used in the distillation, but the entire inflorescence, including the *upper green leaves*. Strictly speaking these should not be included but they mostly are. On the other hand, the woody parts of the plant are not used. In one instance in which a poorly-cut material was used intentionally the yield dropped to 0.5 p.c. However, the properties of the oil, especially its ester content, were the same as those of oil distilled from normal material: $d_{15°}$ 0.8910; $\alpha_D - 8° 13'$; 51.6 p.c. ester; soluble in about 6 vol. and more of 70 p.c. alcohol, with slight turbidity. The inference is that the woody parts contain little oil or none whatever.

According to Lamothe the yield under ordinary conditions amounts to 0.69 p.c., in dry years 1 p.c. More favorable are said to be the results obtained from artificial stands, *viz.,* 0.8 p.c. Compare herewith the statements above made by Schimmel & Co.

Development of the oil in the plant. The changes which the oil undergoes during the development of the plant have been studied by E. Charabot[1]) in connection with three oils, obtained from plants with floral buds, from flowering plants and from plants after the flowering period. The results became apparent from the following tabulation:—

	Oil from plants bearing buds	Oil from flowering plants	Oil from plants after flowering
Specific gravity at 15°	0,8849	0.8854	0.8821
Optical rotation (100 mm.) . .	$- 6° 32'$	$- 6° 48'$	$- 6° 50'$
Linalyl acetate	36.6 p.c.	40.4 p.c.	39.75 p.c.
Free linalool	21.0 p.c.	16.7 p.c.	18.9 p.c.
Free acetic acid in 100 ccm. aqueous distillate	0.5241 g.	0.4716 g.	0.3846 g.

From these data Charabot draws the following conclusions, namely, that during the development of the lavender plant the

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[1]) Compt. rend. 130 (1900), 257.

East of Greenwich

Districts of Production
of
Lavender and Spike Oils
in
SOUTHERN FRANCE.
Scale 1 : 1600000

Explanation:

	Lavender Oil ordinary
	" " fine
	Spike Oil
	Locality with Market of Lavender Oil
	" Production of " Spike Oil
	" Market " Lavender Oil
	Production of Lav: Oil by Schimmel & Co.

MEDITERRANEAN

GOLFE DU LION

SEA

MARSEILLE
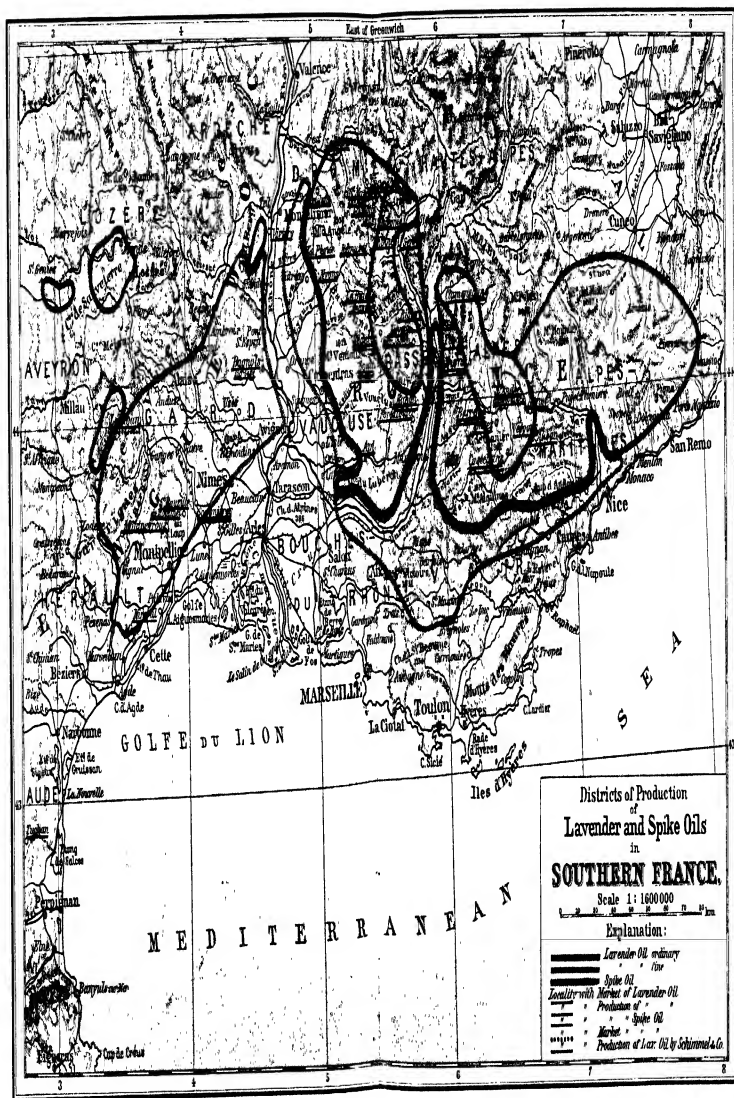
same changes take place as those observed in connection with the bergamot fruit. The linalool, which is produced first, under the influence of free acetic acid is changed into linalyl acetate, which attains its maximum during the flowering period of the plant.

Distribution of Lavender in Southern France. The location of the lavender districts in southern France is indicated on the accompanying map. A study of this map reveals that the best oil with higher ester content is obtained from the higher regions, the less desirable from the lower regions. As to whether the altitude[1]) as such exercises an influence on the composition of the oil remains undecided. A possible explanation for the lower ester content of the oils from lower altitudes may be looked for in the fact that in these lower ranges spike grows together with lavender, as does also the cross between the two which will be described below. Inasmuch as these plants are not always strictly differentiated while gathering material for the stills, the lavender oil of these regions is mixed more or less with spike oil which has a much lower ester content than pure lavender oil.

When lavender and spike grow together crossing of the two species takes place: *la lavande s'aspique,* as the French put it. The cross (*Lavandula fragrans* × *latifolia,* Chatenier; *L. Burnati,* Briq.), which is mostly designated *lavandin*[2]), is also known by other names in southern France; *lavande bâtarde, grosse lavande, badasse, spigoure,* &c. As to the development of its flowers, it is about fourteen days later than lavender proper, a peculiarity that is in harmony with its crossed character of lavender and spike, since the latter flowers even later, namely, early in September. *Lavandin* predominates in the zone of the stone oak and even passes beyond it. A broad band of its occurrence passes through the former Provence, now the Départments Drôme, Vaucluse, Basses-Alpes, &c. to the summits of the hills to the south.

Like all bastards the *lavandin* prospers remarkably well and on account of its luxuriant development endangers the

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[1]) Comp. Jeancard and Satie, Bull. Soc. chim. III. 23 (1900), 549; IV. 3 (1908), 155.

[2]) L. Lamothe, *Lavande et Spic,* 2. Aufl., Le Grand-Serre (Drôme) 1908; Parfum. moderne 5 (1912), 9. Comp. also A. Birckenstock, *Action de l'hybridation sur les essences de lavande et aspic.* Moniteur scientifique de Quesneville, May 1906.

lavender plants proper, depriving them of air and nourishment. It causes worry to see how this cross year after year conquers more territory, all the more since it is avoided by grazing sheep and goats on account of its bitter taste, whereas the genuine lavender is at times a welcome substitute for grass.

In spite of its bitter herbaceous and camphor-like odor which is greatly inferior to that of lavender, considerable quantities of *lavandin* are distilled.   Lamothe[1]) estimates the amount of *lavandin* oil which annually finds its way into the market as about $1/5$ of the total production, *i. e.*, about 12000 kg.   He regrets this fact and warns against the distillation of *lavandin* flowers although with less labor they afford a better yield, for they produce an inferior oil, hence may injure the dominant position of the French lavender oil.   As to the relative yields Lamothe makes interesting comparisons which are herewith reproduced. In the same time which is required to gather 55 kg. of flowers from genuine lavender, it is possible to gather without exertion 400 kg. of *lavandin* blossoms which are much more profuse. Of the latter only 77 to 80 kg. are required to produce 1 kg. of oil, whereas of the genuine lavender plant 145 kg. are necessary.

Concerning the *lavandin* oil itself Lamothe makes the statement that in the samples distilled by himself he found an average ester content of 24 p.c.   Inasmuch as a lavender oil with a 30 p.c. ester content is regarded as low, the inferiority of the *lavandin* oil is clearly apparent.

Lamothe suggests to eliminate this cross from all utilization.

Oils of deviating properties, *i. e.* such as are characterized by a very low ester content of from 20 to 30 p.c. without being adulterated are produced in the Alps along the Franco-Italian border.   According to A. Birckenstock[2]) the annual production is sufficiently high (about 5000 kg.) so that the peculiar properties of these oils warrant consideration.   They have a very fine bouquet, but the "body" is wanting.   The constants of these oils are recorded under Properties on p. 435.

Production. According to Lamothe[2]) the following departments of southern France come into consideration so far as the production

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[1]) Parfum. moderne 5 (1912), 9.

[2]) *Loc. cit.*

of lavender oil is concerned: Drôme with 28 000 kg., Basses-Alpes with 12 000 kg., Vaucluse with somewhat more than 10 000 kg., Ardèche with 200 kg., a total of more than 50 000 kg. In several
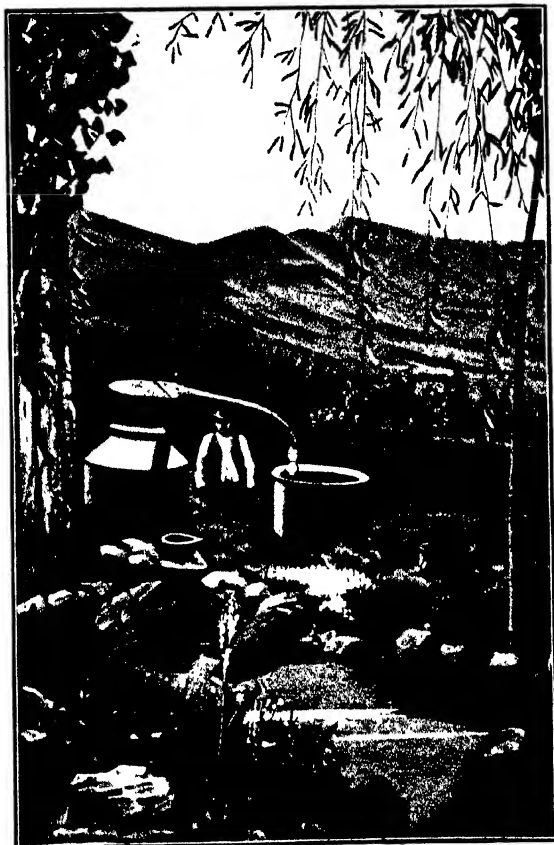
Fig. 33. Distillation of lavender in the vicinity of Séderon.

other departments only small amounts of oil are produced which exert no influence on the market.

In the department Drôme the oil production is distributed over the several cantons as follows: La Motte-Chalançon and Séderon each 4500 kg., Luc-en-Diois 3000 kg., Bordeaux, Saillans,

Rémuzat each 2500 kg., Dieulefit, Nyons, Buis-les-Baronnies each 2000 kg. from the best lavender; in the districts Pierrelotte, Grignan and Saint-Paul-Trois-Châteaux together 2500 kg. of *lavandin* oil. As already stated, the entire department totals an average of 28000 kg. oil.

The principal production centres in the Départment Basses-Alpes are the Lure mountain chain, further Cruis, Mallefoûgasse, Saint Etienne, Banon, Forcalquier, Châteauneuf, Valbelle, Sisteron, the vicinity of *Barrême*, Clumac, Lambruisse, Tortonne, Castellane and Senez.

Cultivation. The cultivation, of lavender in southern France is becoming more and more an object of general interest. Professional journals as well as the daily press are endeavoring to direct the attention of the agricultural population to this new source of industry[1]).

By suitable methods of cultivation at appropriate altitudes, both growth and flower production can be increased. According to E. Zacharewicz[2]) cultivation may undertake to improve a natural lavender field or to proceed with seeds or cuttings (*éclats*).

According to the first plan a natural lavender area is so ploughed during the month of March — more recently a hoe *(houe canadienne)* is employed — so that rows of lavender plants a meter apart result. This results in the destruction of some lavender plants, it is true, but the loss thus suffered is more than compensated by proper cultivation, for the yield is again as great.

On the other hand, a lavender culture may be started with either seeds or growing plants. Seeds are cheaper, but growing plants afford greater returns during the first years thus equalizing the greater initial expense.

Transplanting may be done either in fall or spring. If on account of the altitude there is danger from frost, it should be done in spring. The plants are set out in rows a meter apart, 60 cm. in the row, so that a hectare ($2^1/_2$ acres) requires 16600 plants.

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[1]) Le Réveil Agricole 1907, p. 373, 374 and 389; Rev. de Grasse 50 (1907), No. 35 and 46; 51 (1908), No. 28 and 32. Le Ventoux (Carpentras), 1907, No. 300.

[2]) *Culture de la lavande vraie.* Bulletin mensuel du Syndicat Agricole Vauclusien 23 (1907), 230.

Sowing can be done either in fall or spring. If the winters are not severe fall sowing is preferred. The seeds are placed 2 to 3 cm.

Fig. 35.

Fig. 34.

Distillation of lavender in the vicinity of Séderon (Basses-Alpes).

deep in rows a meter apart. For an area of 1 sq. meter 1 g. of seeds are taken, hence for a hectare 10 kg. are required. Two

cultivations are required, one at the beginning of winter, the other in March. During the latter, the artificial fertilizer which has previously been spread between the rows, is worked under.

According to Lamothe[1]) the best fertilizer is the artificial which increases both the amount of blossoms and the yield of oil. For level areas he recommends a mixture of 100 to 120 kg. soda saltpetre, 300 kg. superphosphate and 100 to 150 kg. kainite. For lavender gardens that are located on slopes the soda saltpetre is replaced by ammonium sulphate (120 to 150 kg.). To those who do not want to apply the artifical fertilizer on account of the expense, Lamothe suggests to plant the lavender rows 1.50 to 2 m. apart and to sow a kind of sweet clover *(Onobrychis sativa,* L., *Leguminosæ),* known as *esparsette,* between the rows. Like the lupine this is ploughed under every two or three years in order to supply the soil with nitrogen. Aside from the fertilizing, a surface cultivation of the soil is required toward the end of March, and a deeper cultivation in longer intervals. In addition, the dry wood and dead plants should be removed twice each year.

In order to insure better financial returns, Lamothe suggests to combine the cultivation of lavender with that of mushrooms. Some farmers are already said to have effected this combination. Inasmuch as the oaks for this purpose are planted at distances of from 7 to 8 m. the intervening space can well be planted with lavender. In the place of the oaks, almond trees or other nut trees can be used.

According to Lamothe, the cutting should not begin too early, not before August, so that the seeds may mature well and may be saved. Inasmuch as they demand a price of from 15 to 20 francs their harvest may add to the financial success. On the other hand, to postpone cutting unnecessarily is not advisable since the September fogs injure the blossoms by facilitating the growth of a fungus about which, as yet, nothing special is known. Rain also is harmful. The flowers should be cut only during dry weather. Weeds are another enemy, especially a species of *Cuscuta* (Ger. *Flachsseide*) which should be exterminated. Sheep and goats also greatly injure the fields.

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[1]) L. Lamothe, *Lavande et Spic.* 2nd ed. Le Grand-Serre (Drôme) 1908.

Fig. 36. Distillation of lavender oil near Escragnolles (Département des Alpes-Maritimes), southern France.

Production of Lavender Oil in England. Compared with the French the English lavender oil industry is of minor significance. Whereas in France the wild plant is mostly used, in England the cultivated plant is exclusively employed. The lavender gardens[1]) are found in Mitcham, County of Surrey, in Carshalton, Beddington and Wallington, also in Canterbury (Kent), Hitchin (Hertfordshire), in Market Deeping (Lincolnshire) and Broadstone (Dorsetshire). The distillation which begins in the early weeks of August, is conducted in the same stills in which that of peppermint has been carried on. The yield is stated to be 0.8 to 1.7 p.c. of the fresh flowers.

So-called Spanish lavender oil is obtained from an unknown species. According to its properties it is to be designated as a spike oil and will be described as such on page 436.

Properties. French lavender oil is either a colorless[2]) or yellowish or greenish-yellow liquid possessing the pleasant characteristic odor of lavender flowers, and a strongly aromatic, slightly bitter taste. $d_{15°}$ 0.882 to 0.896; α_D — 3 to — 9°; $n_{D20°}$ 1.460 to 1.464. At 20° it is as a rule soluble in 2 to 3 and more volumes of 70 p.c. alcohol, occasionally with slight opalescence. Some oils, particularly those obtained by steam distillation (see p. 422 and 435), required up to 10 vol. of 70 p.c. alcohol to effect solution. In individual cases even these solutions are slightly turbid. If in doubt as to the cause of the turbidity, a

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[1]) Additional details about the cultivation and distillation of English lavender may be found in the following publications: E. M. Holmes, Pharmaceutical Journ. III. 8 (1877), 301. — Flückiger and Hanbury, Pharmacographia p. 477; J. C. Sawer, Pharmaceutical Journ. III. 20 (1890), 659 and Odorographia, London 1892, vol. I., p. 356. — Chemist and Druggist 39 (1891), 398. — Pharmaceutical Journ. 58 (1897), 52. — Brit. and Colon. Druggist 84 (1898), 338. — Chemist and Druggist 63 (1903), 825. — Americ. Perfumer 2 (1907), 133. — Chemist and Druggist 72 (1908), 537. — Chemist's and Druggist's Diary 1908, 236. — Pharmaceutical Journ. 83 (1909), 532. — Perfum. Record. 1 (1910), 96; 2 (1911), 231. — Parfum. moderne 3 (1910), 29; 4 (1911), 57. — Bull. Imp. Inst. 9 (1911), 401. — Chemist and Druggist 82 (1913), 399.

[2]) For the most part only the rectified oils are colorless. However, rectification of lavender oil is quite irrational, since it destroys in part the linalyl acetate, its most important constituent. Moreover, rectified oils have invariably a stale odor. (Report of Schimmel & Co. October 1894, 32.)

detailed examination of the oil becomes necessary. For the oils that are readily soluble in 70 p. c. alcohol, it required 5 to 6 vol. of 68 p. c. alcohol, and about 3 to 4 vol. of 69 p. c. alcohol to effect solution according to the ester content. Even then the oils richer in ester show an opalescence that does not disappear upon the addition of more solvent.

The linalyl acetate content of ordinary commercial oils as a rule amounts to 30 to 40 p. c., but in the more rationally steam-distilled oils rises to above 50 p. c. According to the ester content, which is indicative of the value of the oil, lavender oils are grouped into several classes, namely those with about 30 p. c., 35 p. c., 40 p. c. and 50 p. c. and above. Most of the pharmacopœias are content with a 30 p. c. content, some pay no attention whatever to the amount of ester. Oils with less than 30 p. c. linalyl acetate are, for the most part, adulterated. Rarely is the low ester content due to the source of the flowers (see below) or to imperfect methods of distillation whereby part of the ester is destroyed.

In connection with lavender oils, steam-distilled by themselves in southern France, Schimmel & Co.[1]) observed the following properties: —

	Barrême Oils	Sault Oils
$d_{15°}$	0.886 to 0.896	0.885 to 0.891
α_D	$-7°$ to $-9°33'$	-7 to $-8°$
Ester	47 to 56 p. c.	36 to 43 p. c.
Solubility in 70 p. c. alc.	Soluble in 3 to 7 vol. and more, occasionally with opalescence or slight turbidity.	Soluble in 3 to 10 vol., solution mostly clear.

The same firm also reports on an oil[2]) that had been distilled from lavender grown in Miltitz near Leipzig: $d_{15°}$ 0.8888; α_D $-8°40'$; $n_{D20°}$ 1.46010; A.V. 0.5; E.V. 157.6 $=$ 55.1 p. c. of linalyl acetate; with 10 vol. and more of 70 p. c. alcohol it yielded a turbid solution.

As already pointed out on p. 428 the oils produced by water distillation in the Franco-Italian Alps show a specially low ester content. At the same time they are characterized by a low

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[1]) Report of Schimmel & Co. April 1907, 66.

[2]) *Ibidem* October 1909, 73.

specific gravity and a high optical rotation. A. Birckenstock[1]) records the following limit values: d_{15° 0.878 to 0.882; α_D — 8 to — 9°; ester content 20 to 30 p.c.; soluble in 10 to 12 vol. of 60 p.c. alcohol.

Of a similar nature are the data recorded by P. Jeancard and C. Satie[2]) concerning the lavender oils from the Italian Alps; d_{15° 0.8826 to 0.8870; α_D — 6° to — 9° 30′; ester content 20.3 to 29.6 p.c.; soluble in 1.7 to 2.4 vol. of 70 p.c. alcohol and in 2 to 4 vol. of 65 p.c. alcohol. Many oils are soluble even in 60 p.c. alcohol (6 to 8 vol.).

The following observations have been recorded in the laboratory of Schimmel & Co. in connection with an Italian oil distilled in Vinadio (Alpes-Maritimes): d_{15° 0.8824; α_D — 6° 45′; 32.8 p.c. ester; soluble in 3 vol. and more of 70 p.c. alcohol.

Oils of low ester content are also afforded by the so-called *lavandin*, a cross between lavender and spike (see p. 427). Their properties are intermediate between those of lavender and spike, and differ from the Italian oils in that their specific gravity is high and the optical rotation low. In connection with two characteristic *lavandin* oils, Birckenstock *(loc. cit.)* determined the following constants: d_{15° 0.9027 and 0.8995; α_D — 0° 43′ and — 1° 35′; ester content 6.23 and 9.12 p.c.; alcohol content ($C_{10}H_{18}O$) 34.8 and 36.5 p.c.; soluble in 3 vol. of 65 p.c. alcohol. Schimmel & Co.[3]) observed: d_{15° 0.8911; α_D — 3° 25′; 18 p.c. ester; soluble in 2 vol. and more of 70 p.c. alcohol. In connection with *lavandin* oil distilled by himself Lamothe[4]) observed 24 p.c. ester.

Commercial Spanish lavender oil, about the botanical origin of which nothing definite is known, has almost the same properties as oil of spike. It differs from spike oil only in that it is mostly lævogyrate: d_{15° 0.900 to 0.914; α_D lævogyrate up to −5°, exceptionally slightly dextrogyrate, up to + 4°; α_D of the first 10 p.c. of the distillate mostly dextrogyrate, rarely lævogyrate; n_{D20° 1.464 to 1.466; A.V. up to 2; E.V. 5 to 22 = 1.8 to 7.7 p.c. ester computed as linalyl acetate. It is soluble in 1.5

[1]) *Action de l'hybridation sur les essences de lavande et aspic.* Moniteur scientifique de Quesneville, May 1906.

[2]) Bull. Soc. chim. IV. 3 (1908), 155.

[3]) Report of Schimmel & Co. April 1912, 87, footnote.

[4]) Parfum. moderne 5 (1912), 9.

detailed examination of the oil becomes necessary. For the oils that are readily soluble in 70 p.c. alcohol, it required 5 to 6 vol. of 68 p.c. alcohol, and about 3 to 4 vol. of 69 p.c. alcohol to effect solution according to the ester content. Even then the oils richer in ester show an opalescence that does not disappear upon the addition of more solvent.

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[1]) Report of Schimmel & Co. April 1907, 66.

[2]) *Ibidem* October 1909, 73.

60 p.c., is *linalyl acetate.* In addition to the acetic ester of linalool, those of *butyric acid* (analysis of the silver salt)[1]), also of *valeric* and *caproic acids* (analysis of the silver salt)[2]) are present in small amounts. The presence of formic acid could not be detected. *Linalool* is present not only as ester but also in the free state.

Whereas the oil distilled by Schimmel & Co. from dry flowers contained no pinene, fraction 160 to 170° of a large quantity of French oil contained a very small amount of *α-pinene* (m.p. of pinene nitrosochloride 102°; m.p. of pinene nitrolbenzyl-amine 122 to 123°). Of *cineol* also only traces are present. In one case its presence could be detected (hydrogen bromide addition product, iodol reaction) only after the corresponding fraction had been heated with formic acid to destroy the linalool[3]).

If larger amounts of pinene can be isolated, adulteration with turpentine oil may be suspected, more particularly if such suspicion is suported by the determination of the ester content, specific gravity, optical rotation and solubility in 70 p.c. alcohol. On the other hand, the presence of larger amounts of cineol indicate adulteration of the French oil with oil of spike.

Linalool is accompanied in lavender oil by a second alcohol $C_{10}H_{18}O$, *geraniol.* From fraction 110 to 120° (13 mm.) of lavender oil, calcium chloride separated an oil which yielded the diphenyl urethane of geraniol melting at 82°[4]). This alcohol also occurs free as well as in ester form of *acetic, butyric, valeric* and *caproic* acids[2]).

In 1900 Schimmel & Co.[5]) found *cumarin* (m. p. 68.5 to 69.5°) in the oil. From the point of view of the odor this is a not unimportant constituent. Of the other constituents a considerable number were identified in the course of time by Schimmel & Co.[5]).

The lowest fraction contains *furfurol*[6]) (test with aniline hydrochloride), an aldehyde presumably identical with *valeric*

[1]) Report of Schimmel & Co. April 1904, 61.

[2]) *Ibidem* April 1903, 48.

[3]) *Ibidem* October 1893, 26.

[4]) *Ibidem* April 1898, 30.

[5]) *Ibidem* October 1900, 40; April 1903, 48.

[6]) *Ibidem* October 1903, 44.

aldehyde[1]), an alcohol having the properties of *amyl alcohol*[2])
(b.p. 129 to 133°; m.p. of phenylurethane 39 to 41°, presumably
a mixture of several isomers)[3]) and *ethyl-n-amyl ketone* that
is distinguished by its refreshing odor (m.p. of semicarbazone
117 to 117.5°; oxidation to caproic acid)[4]), and of which only
0.2 p.c. are present.

d-*Borneol*[5]), the occurrence of which had already been
pointed out by Bruylants, is present in the free state as well
as acetic ester. It was identified by its oxidation to camphor
(m.p. of oxime 118 to 119°).

According to F. Elze[5]) lavender oil contains *nerol* (m.p. of
tetrabromide 118 to 118.5°; m.p. of diphenylurethane 50°), also
thymol (m.p. 50 to 51 ; m.p. of phenylurethane 107 to 107.5°;
m.p. of nitroso derivative 160 to 160.5°). Inasmuch as an oil
distilled by Schimmel & Co. from Miltitz lavender contained no
trace of thymol this phenol cannot be regarded as a normal
constituent. It must rather be assumed that it entered the oil
examined by him during the process of distillation when a
thymol-containing herb was distilled with the lavender.

The sesquiterpene fraction consists of *caryophyllene* (m.p.
of caryophyllene alcohol 93 to 93.5°; m.p. of phenylurethane
136 to 137°)[6]).

Finally attention may be directed to a phenomenon repeatedly
observed in the laboratory of Schimmel & Co.[2]) during the
investigation of lavender oil. It is the simultaneous occurrence
of the odor of formaldehyde and the formation of a gelatinous,
sticky substance when fraction 78 to 90° (5 mm.), 195 to 215°
(ordinary pressure) is distilled. No explanation has been found
thus far.

English lavender oil has been examined by F. W. Semmler
and F. Tiemann[7]). From the first fraction of this oil they
obtained a tetrabromide melting at 105° thereby proving the

[1]) Report of Schimmel & Co. April 1903, 48.
[2]) *Ibidem* April 1903, 44.
[3]) *Ibidem* October 1903, 42.
[4]) *Ibidem* 43.
[5]) Chem. Ztg. 34 (1910), 1029.
[6]) Report of Schimmel & Co. April 1913, 70.
[7]) Berl. Berichte 25 (1892), 1186.

presence of *limonene*. Fraction 85 to 91° (15 mm.) consisted of l-*linalool,* fraction 97 to 105° of l-*linalyl acetate.* In the highest fraction a *sesquiterpene,* $C_{15}H_{24}$, not further investigated, was found. English lavender oil differs from French oil by its greater *cineol* content[1]), also by its much lower ester content (5 to 10 p.c.).

Examination and Evaluation. The value of lavender oil depends on its linalyl acetate content. It is true that the ester is not the only criterion of the quality of the oil, nevertheless the fragrance and the commercial value of the oil are in direct relation to the amount of ester present, assuming naturally that the oil is a normal distillate and has no empyreumatic odor due to careless preparation. Such an instance is rather improbable since irrational distillation would at the same time result in partial destruction of the ester. Hence, a carefully prepared oil must always reveal a relatively· high ester content. If the linalyl acetate is partly destroyed during distillation the free acid resulting exerts a destructive influence on the linalool and thus interferes with the aroma of the oil in perceptible manner.

Adulteration mostly results in a lowering of the ester content, hence quantitative saponification is absolutely essential in testing an oil.

In order to test for foreign additions, specific gravity, optical rotation and solubility in 70 p.c. alcohol should be ascertained.

Formerly the principal adulterants were turpentine oil, cedar wood oil and oil of spike. Turpentine oil diminishes the ester content and the solubility in 70 p.c. alcohol, also lowers the specific gravity and·can be detected as pinene (see Composition) without difficulty. Cedar wood oil likewise influences solubility and ester content, whereas oil of spike only lowers the ester content. In addition, oil of spike can be recognized by its higher cineol content and by the occurrence of the *d*-camphor.

More difficult of detection, hence more dangerous than the adulterants already mentioned, are such substances which seemingly increase the linalyl acetate·content. They are the same esters previously enumerated under oil of bergamot, namely, terpinyl

¹) Report of Schimmel & Co. October 1894, 32.

and geranyl acetate, also the ethyl esters of succinic, oxalic, tartaric and citric acids. The analytical method for their detection has been described under Bergamot oil on pp. 68 to 71 and need not be repeated here. When fractionally saponified (p. 69) pure bergamot oil reveals differences in the saponification values of 4 at most, whereas the difference between saponification and acid value II (p. 72) in general does not exceed 3. Somewhat greater differences may be due to resinification. In doubtful cases the test should be repeated with oil rectified with water vapor.

Occasionally other adulterants of lavender oil have been observed. To describe them individually would lead too far. Suffice it to include them in the following enumeration with references to the original literature.

. Up to the present time the following foreign additions have been found: rosin (colophony?)[1], turpentine oil[2][3][5], oil of spike[2][3][5]), Spanish sage or lavender oil[2][3][4][5]), rosemary oil[2][3]), benzoic acid[5]), salicylic acid[6]), succinic acid ester[7][5]), citric acid ester[9]), glyceryl acetate[10][11][12][14]), terpinyl acetate[12][14]), esters of fatty acids from cocoanutoil[13]), phthalic acid ester[13]), alcohol[8]) and petroleum[3]).

768. Oil of Spike.
Oleum Spicæ.   ·   Spiköl.   Essence d'Aspic.

Origin. *Lavandula Spica,* D.C. *(Lavandula Spica* var. β., L.; *Lavandula vulgaris* β., Lam.; *Lavandula latifolia,* Vill., Ger. *Spik-*

[1]) Report of Schimmel & Co. October 1900, 42.

[2]) *Ibidem* October 1905, 42.

[3]) *Ibidem* October 1904, 51.

[4]) *Ibidem* April 1908, 63.

[5]) *Ibidem* April 1902, 46.

[6]) E. Weber, Chem. Ztg. 26 (1902), 875.

[7]) Report of Schimmel & Co. April 1897, 24.

[8]) *Ibidem* April 1905, 52, 53, 54.

[9]) C. T. Bennett, Chemist and Druggist 69 (1906), 691. — Report of Schimmel & Co. April 1907, 66.

[10]) P. Jeancard and C. Satie, Bull. Soc. chim. IV. 3 (1908), 155.

[11]) Report of Schimmel & Co. October 1911, 57.

[12]) *Ibidem* October 1912, 75.

[13]) F. Delphin, Svensk Farmaceutisk Tidskrift 1908, No. 22; 1912, No. 5; Report of Schimmel & Co. April 1912, 88.

[14]) Report of Schimmel & Co. April 1912, 88.

lavendel) is distributed in the Mediterranean countries in about the same manner as the genuine lavender. In southern France it grows in the lower regions up to 700 m as highest altitude, where *Lavandula vera*, D.C. begins. In Spain it is especially common.

Spike (French *lavande mâle, grande lavande, spic* or *aspic*) is larger than lavender. The stems often have numerous branches and attain a height of 80 to 90 cm. The floral bracts are lineal and as long as the calyx, which is whitish. The plant grows at the lower altitudes on dry, sunny and protected slopes[1]). It is sturdy and makes no special demands upon the soil, but prefers a deep, if possible alluvial soil, since its tap roots sink to a depth of 30 to 40 cm. The spike flowers are fully developed about 3 weeks later than those of the lavender, namely toward the end of August. On account of their high growth the harvest is less laborious than that of lavender. On the other hand spike shows less tendency to spread, so that the individual plants can develop well and are of longer duration. It should also be mentioned that the strong odor of the flowers and the bitter taste of the leaves protects the spike against being devoured by grazing animals. A cross between spike and lavender has been described on p. 427.

As yet no attempts have been made to cultivate spike, although the few demands which the plant makes on the soil should render this easy. However, it might scarcely pay to cultivate spike where any other economic plant will grow.

For the distribution of spike in France, see the map on p. 426 accompanying oil of lavender.

Distillation. In Spain the oil is produced like oil of thyme, in southern France in like manner as lavender oil and, as a rule, by water distillation over direct fire. The yield is said to be only 0.5 to 0.62 p. c.[2]) Steam distillation however, yields more than 1 p. c.

For the sake of comparison Schimmel & Co.[3]) have distilled spike in southern France over direct fire as well as with steam. The results are recorded in the following table: —

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[1]) L. Lamothe, *Lavande et Spic.* 2nd ed. Le Grand-Serre (Drôme) 1908.
[2]) Laval, Journ. de Pharm. et Chim. V. 13 (1886), 599.
[3]) Report of Schimmel & Co. November 1908, 114.

	$d_{15°}$	α_D	α_D of the first 10 p.c.	E.V.	Solubility in alcohol of		
					60 p.c.	65 p.c	70 p.c
1. Steam[1] distillation	0.9075	$0°49'$	$+3°16'$	7.0	insoluble in 20 vol.	1:3.3 vol.	1:2 vol.
2. Water[2] distillation	0.9078	$+0°42'$	$+3°7'$	9.4	1:6.5 to 7 vol.	1:3.5 to 4 vol.	1:2 vol.
3. „	0.9050	$0°28'$	$+1°40'$	5.1	1:6 to 7 vol.	1:3.5 vol.	1:2 vol.
4. „	0.9054	$-0°26'$	$+2°1'$	6.1	1:8 vol.	1:3 to 3.5 vol.	1:2 vol.
5. „	0.9058	$-0°45'$	$+2°44'$	10.1	1:8 vol.	1:3 to 3.5 vol.	1:2 vol.
6. „	0.9052	$-0°43'$	$+2°30'$	11.1	1:8 vol.	1:3 to 3.5 vol.	1:2 vol.

The difference in the solubility, as becomes apparent, is due to the method of distillation. Whereas all oils obtained by water distillation are soluble even in 60 p.c. alcohol, this does not hold for the oils obtained by steam distillation. Less ready solubility has also been observed in connection with oils distilled over direct fire. This decreased solubility is probably attributable to the fact other plants such as *Satureia montana*, L., *Calamintha officinalis*, Mœnch, *Sideritis romana*, L., *Teucrium Polium*, L. etc. are distilled with spike[3]).

Production. FRENCH SPIKE OIL. In 1908 L. Lamothe[4]) estimated the annual production of southern France at about 25000 kg. At the price of from 8 to 12 francs per kg. this represents an average value of 250000 francs. In 1913 it commanded 15 fr. per kg. For the production of spike oil the following departments come into consideration: Drôme (3000 kg.), Vaucluse, Basses-Alpes, Bouches du Rhône, Var, Alpes-Maritimes, Gard, Hérault, Aude and others.

SPANISH SPIKE OIL. For the past 15 to 20 years it is principally the Spanish oil of spike, falsely called Spanish lavender oil at times, that is to be found in commerce. It is produced in the provinces of Granada, Valencia, Murcia and Cordoba. As in France it is obtained from *Lavandula Spica*, D.C. (Spanish *Espliego*)[5]). The amount of oil produced annually is estimated at at least 50000 kg.

[1]) Yield 1.1 p.c.
[2]) Yield 0.98 p.c.
[3]) Report of Schimmel & Co. April 1912, 104.
[4]) *Loc. cit.*
[5]) Report of Schimmel & Co. October 1911, 85.

On one occasion a small amount of spike oil of good quality was produced in Dalmatia[i]).

Properties. Spike oil is a yellowish liquid with a camphor-like odor that reminds both of lavender and rosemary. Concerning its optical rotation, the following generalization should be noted: As a rule it is dextrogyrate, but occasionally unobjectionable oils with lævorotation have been observed. Thus Schimmel & Co.[2]) have observed $-0'49'$ (comp. table on p. 443) in connection with an oil distilled in their factory in Barrême (Alpes-Maritimes, southern France). For an oil distilled from dried Spanish flowers they observed $-2°20'')$. Two Dalmatian oils that were unquestionably genuine deviated $-0°10'$ and $-0°53'')$. Hence lævogyrate spike oils may be pure, but as a rule are adulterated or replaced by other similar oils of different botanical origin. In doubtful cases it is well to question such oils. In all cases the first 10 p.c. obtained by fractionation in a Ladenburg flask (see vol. I p. 566) should be dextrogyrate.

FRENCH SPIKE OIL. $d_{15°}$ 0.905 to 0.9176; α_D as a rule dextrogyrate, up to $+6°44'$, in very exceptional cases lævogyrate, up to about $-2°$; α_D of the first 10 p.c. of the distillate dextrogyrate, up to $+10°40'$, occasionally higher, occasionally lower than the original rotation, $n_{D20°}$ 1.464 to 1.468; A.V. up to about 2; E.V. 3 to 21, mostly not over 10; E.V. after acetylation 102 to 112 — 30.4 to 36.9 p.c. $C_{10}H_{18}O$[3]); soluble in 1.7 to 3 vol. and more of 70 p.c. alcohol. Good oils distilled according to the common method with water are soluble in even 60 p.c. alcohol[4]) (5 to 20 vol.) or in 65 p.c. alcohol[5]) (3 to 5 vol.).

According to A. Birckenstock[6]) the various French oils distilled in the several spike districts yield oils that differ from

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[1]) Report of Schimmel & Co. October 1911, 85.

[2]) *Ibidem* November 1908, 116.

[3]) Acetylated according to regular method without dilution. Inasmuch as the oil contains linalool, the addition of 4 vols. of xylene would have given higher (abt. 10 p.c.), *i. e.* more correct, values. (Comp. vol. I, p. 578.)

[4]) The oils obtained by steam distillation which, however, have not as yet appeared in commerce, appear to be less readily soluble in alcohol. (Comp. table on p. 443.)

[5]) E. J. Parry and C. T. Bennett, Chemist and Druggist **63** (1903), 1011.

[6]) Moniteur scientifique de Quesneville 1906, 355; Report of Schimmel & Co. October 1906, 74.
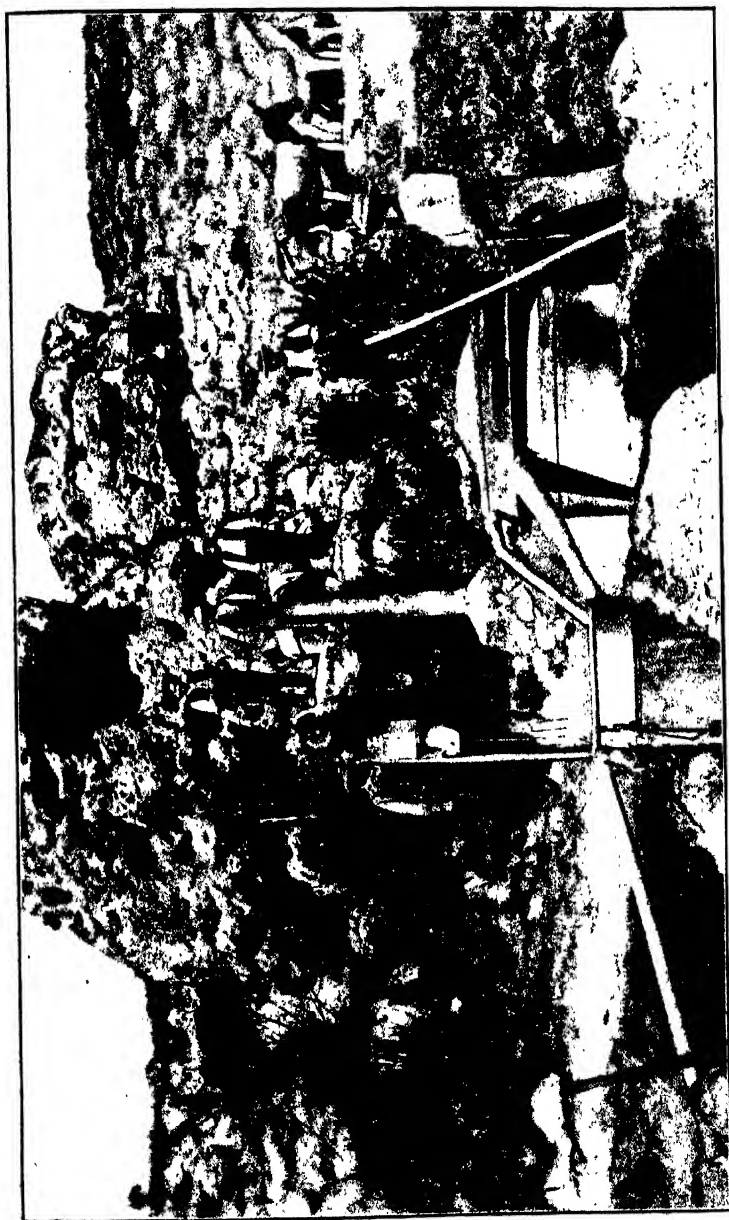
each other. He recognizes seven groups: Ardèche, Hérault, Drôme, Gard, Basses-Alpes, Alpes-Maritimes and Var. In his opinion the first group represents the spike oil type proper with the following properties: $d_{15°}$ 0.918 to 0.921; $\alpha_D + 7°48'$ to $+9°36'$[1]); α_D of the first 10 p.c. of the distillate $+8$ to $+10°$; ester content 4 to 5 p.c.; alcohol content 21 p.c.; soluble in 3 vol. of 67 p.c. alcohol. The group Var, on the other hand, approximates the lavender oil type with the following properties: $d_{15°}$ 0.9035 to 0.905; $\alpha_D - 1°10'$ to $\pm 0°$; α_D of the first 10 p.c. of the distillate $+2°$; ester content 2 to 3 p.c.; alcohol content 20 to 32 p.c.; soluble in 5 to 6 vol. of 60 p.c. alcohol. The other groups occupy intermediate positions. Specific gravity and optical rotation decrease, whereas alcohol content and solubility in alcohol increase. At the same time a change in the alcoholic constituents takes place; the borneol which predominates in the "Ardèche" type giving way more and more to linalool and geraniol.

SPANISH SPIKE OIL. $d_{15°}$ 0.904 to 0.922; $\alpha_D - 4°43'$ to $+15°47'$ rarely above $+8°$; α_D of the first 10 p.c. of the distillate up to $+14°$, as a rule not above $+8°$; $n_{D20°}$ 1.46506 to 1.46535; A. V. up to 1.8; E. V. 4.6 to 26.5, mostly below 20; E. V. after acetylation 84 to 112 $=$ 24.7 to 33.6 p.c. $C_{10}H_{18}O$[2]); soluble in 1.5 to 2.5 vol. of 70 p.c. alcohol, the diluted solution being slightly opalescent in individual instances.

Schimmel & Co.[3]) obtained from Spain a lot of spike flowers the botanical derivation of which from *Lavandula Spica*, D.C. (*L. latifolia*, Vill.) was established by a special investigation. Upon distillation with water vapor it yielded 1.9 p.c. of a brownish-yellow oil with the following constants: $d_{15°}$ 0.9100; $\alpha_D - 2°20'$; α_D of the first 10 p.c. of distillate $+1°10'$; $n_{D20°}$ 1.46823; A. V. 3.7; E. V. 7.0. The oil was soluble in 2 vol. of 70 p.c. alcohol, upon addition of more than 4 vol. of solvent opalescence was produced by the separation of paraffin.

[1]) This statement is not in harmony with other observations on spike oil according to which both specific gravity and optical rotation are lower. See above.

[2]) Acetylated according to regular method without dilution. Inasmuch as the oil contains linalool, the addition of 4 vols. of xylene would have given higher (abt. 10 p.c.), *i. e.* more correct, values. (Comp. vol. I, p. 578.)

[3]) Report of Schimmel & Co. October 1911, 85.

DALMATIAN SPIKE OIL. Two oils produced in Dalmatia had the following properties[1]; $d_{15°}$ 0.9033 and 0.9022; α_D 0°53′ and — 0°10′; α_D of the first 10 p.c. of distillate + 0°16′ and + 2°14′; A. V. 0.9 and 0.9, E. V. 5.6 and 5.4; soluble in 5 and 4 vol. respectively of 60 p.c. alcohol, and in 3 and 2 vol. of 70 p.c. alcohol.

Composition. The first constituent of spike oil to be established with certainty is *camphor*[2]). Although the earlier investigators claim to have found it in lavender oil this substance, as shown in the preceding chapter, does not occur in genuine lavender oil. It may be assumed, therefore, that one does not go amiss in stating that the earlier investigations were carried out with spike oil and not with lavender oil. In addition to camphor, G. Bruylants[3]) also found *borneol* in oil of spike.

A complete investigation of the oil was made by G. Bouchardat alone[4]), partly in conjunction with R. Voiry[5]). After repeated fractionations an insignificant amount (0.2 to 0.25 p.c.) of an oil boiling at 160" was obtained, which, when hydrogen chloride was passed into it, yielded a solid hydrochloride melting at 129°. Boiled with alcoholic potassium acetate this was decomposed for the most part and yielded dextrogyrate camphene which congealed in the cold. As to whether d-α-pinene is present in the oil together with d-*camphene* could not be ascertained with certainty. Bouchardat is of the opinion that that part of the solid hydrochloride which remains unchanged after a brief heating with alcoholic potassium acetate is pinene hydrochloride. Fraction 175°, which constitutes about 10 p.c. of the oil, congealed in a freezing mixture and consisted of *cineol*, $C_{10}H_{18}O$. Its hydrochloride, also the cinnabar-red dibromide $C_{10}H_{18}OBr_2$ were prepared.

The fraction that passed over near 200" proved to be a mixture of l-*linalool,* d-*camphor,* and d-*borneol.*

[1]) Report of Schimmel & Co. October 1911, 84.
[2]) R. Kane, Journ. f. prakt. Chem. 15 (1838), 163. — A. Lallemand, Liebig's Annalen 114 (1860), 198.
[3]) Chem. Zentralbl. 1879, 616.
[4]) Compt. rend. 117 (1893), 53 and 1094.
[5]) *Ibidem* 106 (1888), 551.

The *linalool* (b. p. 198 to 199°; $\alpha_D - 16' 44'$) was converted into geranyl acetate by boiling with acetic acid anhydride. The oxime obtained from the *camphor* had all the properties of ordinary camphor oxime. The *borneol*, having been separated from the camphor by means of benzoic acid anhydride, was also dextrogyrate.

Spike oil may also contain *terpineol*. At least Bouchardat obtained dipentene dihydrochloride by passing hydrogen chloride into a fraction having the boiling point of terpineol. This does not necessarily indicate terpineol for the formation of this hydrochloride may also have been due to the presence of linalool or geraniol. However, positive proof of the presence of geraniol has not yet been brought. With the fraction boiling between 145 and 160° in vacuum and having the odor of geraniol, hydrogen chloride yielded a liquid chloride with the properties of geranyl chloride[1]. The analysis of the highest fraction, boiling at 250° yielded results corresponding with the formula $C_{15}H_{24}$. Hence a sesquiterpene is very likely present.

Examination. The presence of turpentine oil, with which spike oil is most frequently adulterated, is indicated by the lowering of the specific gravity. If French turpentine oil is present in larger amounts it reveals itself by the change in the angle of rotation to the left. If the added amount of this oil is so small as simply to lower the angle of rotation without changing its direction, and if both the specific gravity and solubility of the oil are suspicious, distillation of the first 10 p.c. of the oil and the determination of the optical rotation of this lowest fraction should be resorted to. The lowest fraction of spike oil is almost invariably dextrogyrate, whereas even a moderate addition of French turpentine oil causes lævorotation. Moreover, the quantity of terpenes boiling at about 160° is very small in genuine spike oil. Hence, if larger amounts of dextrogyrate terpenes distill

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[1] Geranyl chloride prepared in this manner is, according to F. Tiemann (Berl. Berichte **31** [1898], 832), not a chemical unit but a mixture of several isomeric chlorides. Compare also additional work on geranyl chloride by J. Dupont and L. Labaune in the *Berichte von* Roure-Bertrand Fils October 1909, 21, April 1910, 42, furthermore by M. O. Forster and D. Cardwell in Journ. Chem. Soc. **103** (1913), 1338.

ver, the oil may be declared as having been adulterated (American
ırpentine oil, camphor oil).

The detection of the presence of rosemary oil is more
ifficult. However, it is used much less frequently as adulterant
ince the difference in price makes its addition less profitable.
pecific gravity, optical rotation and boiling temperature are
lmost the same for both oils. Only the solubility in 70 p.c.
nd more particularly 60 p.c. alcohol differs. Mixtures of the
ʋo oils frequently dissolve in 2 to 3 vol. of 70 p.c. alcohol, but
ie clear solution becomes turbid upon the further addition of
ie solvent.

Difficult, likewise, is the detection of the addition of Spanish
il of sage. (See this.)

769. Oil of Lavandula Stœchas.

Origin and Production. *Lavandula Stœchas*, L. is known in
ıpain as *Romero santo* (Ger. *heiliger Rosmarin*), also as
`antueso. Its volatile oil, like that of *Lavandula dentata*, L.,
ɔ prepared as a domestic remedy in the following manner. The
owering plants, with the inflorescences inverted are suspended
ı flasks. These are closed and exposed to the sun's rays for
time. At the bottom of the flasks there collects a mixture
f water and volatile oil that is used to check bleeding, for the
ʋashing of wounds and as remedy against eruptions.

Occasionally, however, the oil is produced in ordinary stills.
ıuch a product produced in Spain, the botanical origin of which
·om *Lavandula Stœchas* was established by a special investigation,
ʋas examined by Schimmel & Co. who found the following
onstants: d_{15° 0.9317; α_D — 39° 40′; n_{D20° 1.47099; A.V. 2.8;
⸫V. 101.7 = 35.6 p.c. ester $CH_3COOC_{10}H_{17}$. Very similar pro-
erties were revealed by a second sample; d_{15° 0.9340; α_D — 40°;
$_{D20^\circ}$ 1.47058; A.V. 3.3; E.V. 108.8 = 38 p.c. ester $CH_3COOC_{10}H_{17}$.
ɔoth oils were soluble in 3.5 vol. and more of 70 p.c. alcohol.
`heir odor reminded of that of hyssop. Unfortunately only small
mounts of both samples were available. Nevertheless, it was
etermined that they were rich in *cineol*. Furthermore, a *ketone*
ʋith a minty, camphor-like odor (m.p. of semicarbazone 224°),

possibly identical with pinocamphone, also a strongly lævogyrate *alcohol* ($\alpha_D - 115°50'$) were isolated[1]).

770. Oil of Lavandula dentata.

The oil of *Lavandula dentata*, L. is similar to that of *Lavandula Stœchas*, but may be differentiated by its odor which reminds strongly of that of rosemary oil and camphor. Other points of difference are the dextrorotation and the low ester content. What has been said of production and use of the oil of *Lavandula Stœchas* applies here as well. It should be added, however, that in addition to its production in Spain, it is occasionally distilled in southern France.

Properties. From the dry flowers Schimmel & Co.[2]) obtained 0.755 p.c. of oil of a yellowish-brown color and camphor-like odor. $d_{15°} 0.9620$; $\alpha_D + 35°30'$; $n_{D20°} 1.47909$; A.V. 5.16; E.V. 13.1; E.V. after acetylation 67.9; soluble in 2 vol. and more of 70 p.c. alcohol, the diluted solution becoming opalescent because of the separation of paraffin. So far as oils distilled in Spain and southern France are concerned, their properties fluctuated between the following limits[3]): $d_{15°} 0.9420$ to 0.9531; $\alpha_D + 32°6'$ to $+44°46'$; $n_{D20°} 1.46842$ (one determination); A.V. 1.4 to 1.8; E.V. 12.7 to 24.1; soluble in 2 vol. of 70 p.c. alcohol, additional solvent causing slight opalescence in individual cases.

Composition. As constituents of an oil distilled by themselves Schimmel & Co. identified d-*camphor* (m. p. 175 to 175.5°; m. p. of oxime 117 to 118°; m. p. of semicarbazone 231°) and d-*fenchone* (m. p. of oxime 165°). Possibly fenchyl alcohol is also present.

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[1]) Observations made in the laboratory of Schimmel & Co. An oil mentioned in their *Bericht* October 1889 (p. 54) as from *Lavandula Stœchas* ($d_{15°} 0.942$; boiling temperature 180 to 245°) in all probability was derived from *Lavandula dentata*.

[2]) Report of Schimmel & Co. October 1905, 40; April 1908, 62; April 1915, 28. The oil mentioned in the *Bericht* for October 1889, 54, as having been obtained from *Lavandula dentata* was possibly derived from *Lavandula Stœchas*, L.

[3]) Observations made in the laboratory of Schimmel & Co.

771. Oil of Lavandula pedunculata.

Portuguese oil obtained from *Lavandula pedunculata*, Cav. is described as follows by Schimmel & Co.[1]: —

The oil possessed an odor not at all pleasant and difficultly definable, hence may be of no practical value. $d_{15°} 0.939$; $\alpha_D - 44°54'$. It dissolves in equal parts of 80 p.c. alcohol to a clear solution. The high saponification value 111.7 corresponds to 39 p.c. of the acetic ester of an alcohol $C_{10}H_{18}O$. When the saponified oil was distilled with steam a light yellow liquid passed over. The first fraction contained *cineol* which was identified by means of its iodol derivative. The odor of this fraction further suggests the presence of thujone.

772. Oil of Lavandula Burmanni.

From the Indian Institute of Science in Bangalore Schimmel & Co.[2] received small amounts of two distillates from *Lavandula Burmanni*, Benth. The one had been obtained from the leaves, the other from the flowers.

The *leaf oil* was of yellow color and had a citral-like odor. $d_{15°} 0.9131$; $\alpha_D - 0°40'$; A. V. 9.9; E. V. 36.3; soluble in 1.5 vol. and more of 70 p.c. alcohol.

Totally different were the properties of the light-brown *flower oil:* $d_{15°} 0.9309$; $\alpha_D + 1°40'$; A. V. 1.9; E. V. 115.7; soluble in 1.5 vol. and more of 80 p.c. alcohol, but yields only turbid solutions with 10 vol. of 70 p.c. alcohol. Inasmuch as the oil had a distinct fenchone odor, an attempt was made to characterize this ketone. After treatment with potassium permanganate for the purpose of removing the more readily oxidizable constituents, but very little oil remained which possessed a strong *fenchone* odor. It yielded a small amount of oxime melting at 160°. Whether the substance represented active fenchone (m. p. of oxime 164 to 165°) or the optically inactive form (m. p. of oxime 158 to 160°) it was impossible to ascertain with certainty because of the small amount of material.

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[1] Report of Schimmel & Co. October 1898, 31.

[2] *Ibidem* October 1913, 111.

773. Marrubium Oil.

H. Haensel[1]) describes two marrubium oils: That from the herb of *M. album* was obtained with a yield of 0.05626 p.c., was solid, m. p. 17.5°, d 0.9414; that from the herb of *M. nigrum* with a yield of 0.036 p.c., solid, m.p. 16.5°, d 0.934.

Formerly the leaves of *M. vulgare*, L. were official as *Herba Marrubii albi*.

774. Oil of Lophanthus rugosus.

The genus *Lophanthus* (family *Labiatæ*) comprises 6 to 8 species, which are natives of North America and eastern Asia. Whereas *L. anisatus* (see below)[2]) is a North American plant, *L. rugosus*, Fisch. et Mey. grows wild in eastern Asia and is also cultivated, attaining a height of 1.20 m. Upon distillation P. de Vilmorin and F. Levallois[2]) obtained a yield of about 0.23 p.c. (computed with reference to the fresh herb?). The flowering branches contain somewhat more oil, up to 0.5 p.c. The oil is an amber-yellow liquid which is miscible in all proportions with 95 p.c. alcohol, also is soluble in 1.2 vol. of 90 p.c. alcohol, 4.5 vol. of 85 p.c. alcohol and 23 vol. of 70 p.c. alcohol. d 0.962 to 0.967; $[\alpha_D] + 4.89$ to $+ 6.19°$; S.V. 3.7; S. V. after acetylation 7.4. The oil reacts faintly with bisulphite. About 8 p.c. distill between 60 and 63° (10 mm.), 2 p.c. between 63 and 90° (10 mm.), 86 p.c. between 90 and 94° (10 mm.) and about 4 p.c. above 100° with partial decomposition. *Methyl chavicol* appears to be the principal constituent (characterized by converting it into anethol melting at about 20°). The fraction that boiled around 60° (10 mm.) presumably contained d-*limonene* (b.p.178°; $d^{15°}$ 0.8494; $\alpha_D + 106.8°$; m. p. of tetrabromide 104°; m. p. of nitrosochloride 103° and 105° respectively. Upon purification of the nitrosochloride a fraction was obtained that melted at 154° the corresponding hydrocarbon of which has not yet been determined.

775. Oil of Lophanthus anisatus.

The herb of *Lophanthus anisatus*, Benth. (*Agastache fœniculum*, [Pursh] O. Kuntze) has an odor of esdragon. From the

[1]) Pharm. Ztg. 47 (1902), 74.
[2]) Bull. Soc. chim. IV. 15 (1914), 342.

botanical garden in Marseilles Schimmel & Co.[1]) obtained a small lot of the lophanthus herb which, upon distillation with water vapor, yielded 0.11 p.c. of a brownish-green oil with a pleasant, anise-like odor. It had the following constants: d_{15° 0.9640; n_{D20° 1.51655; A.V. 2.8; E.V. 14.0; soluble in 0.5 to 1 vol. and more of 90 p.c. alcohol. On account of the dark color of the oil its optical rotation could not be determined.

Distilled under diminished pressure (3 mm.) about 80 p.c. distilled constantly at 68°. Further investigation of this fraction revealed that it consisted exclusively of *methyl chavicol* which, therefore, is the principal constituent of lophanthus oil. Its identity with methyl chavicol was revealed on the one hand by its physical constants (b.p. 215 to 216°; d_{15° 0.9663; n_{D20° 1.51966); on the other hand by converting it into anethol upon boiling with alkali (d_{20° 0.9848; n_{D20° 1.55800).

An oil previously examined by Schimmel & Co.[2]) was obtained from North America. d_{20° 0.943; α_D —7′ 10′.

776. Catnip Oil.

The oil of catmint or catnip, *Nepeta Cataria,* L., which has been introduced into North America from Europe[3]), has a minty and camphor-like odor that is not pleasant. d 1.041 [4]).

A Sicilian oil of *Nepeta,* the exact botanical origin of which was not determined, has been examined by J. C. Umney and C. T. Bennett[5]), who found the following constants: d_{18° 0.927; α_D +12°; total alcohol content (menthol) 22.2 p.c.; ester content (menthyl acetate) 3.3 p.c.; soluble in 2 vol. of 70 p.c. alcohol. The oil appears to contain small amounts of a ketone possibly menthone or pulegone.

[1]) Report of Schimmel & Co. October 1913, 73.

[2]) *Ibidem* April 1898, 53.

[3]) Alice Henkel, U. S. Dept. of Agriculture, Bureau of Plant Industry, Bull. No. 219; Report of Schimmel & Co. April 1912, 149.

[4]) Report of Schimmel & Co. October 1891, 51.

[5]) Pharmaceutical Journ. 75 (1905), 861. — Chemist and Druggist 67 (1905), 970.

777. Oil of Nepeta Nepetella.

In the vicinity of Saint Auban (Maritime Alps) the labiate *Nepeta Nepetella,* L. occurs abundantly [1]). It possesses a peculiar peppermint-like odor. At the close of the flowering season the oil was distilled with a yield of 0.0598 p.c. It was heavier than water and constituted a yellow, somewhat viscid liquid with the following properties: $d_{20°}$ 1.03984; $d_{82°}$ 1.02536; $\alpha_{D} + 15° 12'$; α_{D} of the acetylated oil $+17° 20'$; A.V. 45.5; E.V. 245,7; E.V. after acetylation 314.5; soluble in 2 vol. of 70 p.c. alcohol, turbidity resulting upon the addition of more solvent. From the oil a solid substance having the odor of menthol was isolated. The saponification lye, when rendered acid, yielded an oil that reminded of both caprylic and valeric acids. A part of the oil combined with bisulphite.

778. Oil of Nepeta Glechoma.

From the dried herb of *Nepeta Glechoma,* Benth. *(Glechoma hederacea,* L., Ger. *Gundermann)* Schimmel & Co. [2]) obtained 0.03 p.c. of a volatile oil that was dark green in color and the odor of which was not pleasant and was difficult to define. $d_{15°}$ 0.925.

H. Haensel [3]) likewise distilled the dry herb and obtained 0.064 p.c. It was dark brown in color intermingled with solid particles and had a penetrating odor which was not pleasant. $d_{21°}$ 0.9296; A.V. 0; S.V. 111. It contained traces of an aldehyde or ketone.

779. Oil of Lamium album.

From the dry herb of *Lamium album,* L. (Ger. *Taubnessel)* H. Haensel [4]) obtained 0.537 p.c. of a dark colored oil which in the cold separated crystalline particles.

780. Oil of Sage.

Oleum Salviæ. — Salbelöl. — Essence de Sauge.

Origin. The somewhat half-shrub-like labiate *Sàlvia offici-nalis,* L. is indigenous to the countries north of the Mediterranean

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[1]) Berichte von Roure-Bertrand Fils October 1911, 41.

[2]) Report of Schimmel & Co. April 1894, 55.

[3]) Apotheker Ztg. 23 (1908), 279.

[4]) *Ibidem* 26 (1911), 388.

and is being cultivated in many countries with temperate climate for ornamental and medicinal purposes.

Production. For the distillation of the oil on a large scale the wild plant which grows abundantly in Dalmatia is employed. The distillation is either conducted on the spot, or the factories purchase the dry herb, strongly compressed in large bales bound with iron bands. The oil yield of Dalmatian leaves amounts to 1.3 to 2.5 p.c. A distillation of German leaves yielded 1.4 p.c. of oil.

Since ·a number of years Spanish oil of sage is to be found on the market. Its botanical origin has not been established with certainty.

Properties. DALMATIAN OIL. It is a yellowish or greenish-yellow liquid with the peculiar odor of the herb, which reminds both of tansy and camphor. $d_{15°}$ 0.915 to 0.930; $\alpha_D + 2°$ to $+ 25°$; n_{D20} 1.458 to 1.468; A. V. up to 2; E. V. 6 to 17; E. V. after acetylation 40 to 60; soluble in 1 to 2 vol. and more of 80 p.c. alcohol, of 70 p.c. alcohol 3 to 12 vol. are required to effect solution, but the solutions are not always clear.

The influences which season and the quality of the material distilled exert on the oil have been shown by two authentic Dalmatian oils[1]. Whereas one of the oils, which had been distilled from dry sage in August had all the properties of a normal oil ($d_{15°}$ 0.9165; $\alpha_D + 25°$; $n_{D20°}$ 1.45871; A.V. 9.3); the other which had been distilled from fresh herb in May, had a much lower specific gravity ($d_{15°}$ 0.9111) than is otherwise observed in connection with Dalmatian oils. The other constants were the usual ones: $\alpha_D + 20° 22'$; A.V. 1.0; E.V. 10.3.

SPANISH OIL[2]. Spanish oil of sage has an odor differing somewhat from that of the Dalmatian oil and related to that of rosemary. $d_{15°}$ 0.910 to 0.933; $\alpha_D - 17$ to $+ 20°$; A.V. up to 1.0; E.V. 5 to 44; mostly more than 15; E.V. after acetylation 40 to 75; soluble in 0.5 to 2 vol. and more of 80 p.c. alcohol, occasionally in individual cases with opalescence.

[1] Report of Schimmel & Co. October 1911, 80.
[2] For other oils described in the literature as sage oils see Oil of *Salvia triloba,* pp. 458 and 459.

Composition. Upon fractionation of a German[1]) oil of sage, H. Seyler[2]) obtained 1 to 2 p.c. that boiled below 155°, which after repeated distillation over sodium was resolved into three parts. The lowest fraction boiled between 142 to 145° (d_{20}, 0.80; n_D 1.4438; $\alpha_D + 1° 40'$) and upon analysis yielded results corresponding with $C_{10}H_{18}$. This hydrocarbon which was named *salvene,* yielded upon oxidation with potassium permanganate an acid in almost quantitative amounts, whose semicarbazone,

$CH(CH_3)_2$
|
C
H_2C / \ CH_2
HC \ / CH_2
$CH \cdot CH_3$.
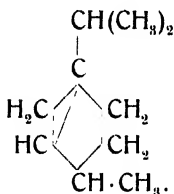
$C_{10}H_{16}O_2CON_3H_3$, melted at 204° and which possibly is identical with β-tanacetone keto-acid (β-thujaketonic acid).

Salvene presumably has the constitutional formula of a dihydrotanacetene. See accompanying formula.

From the first fraction of a Spanish sage oil no salvene could be isolated.

From the lævogyrate fraction boiling at 156 to 158° W. A. Tilden and W. A. Shenstone[3]), also M. M. P. Muir and S. Sugiura[4]) obtained a nitrosochloride. By converting it, according to Wallach, into nitrosopinene[5]) (m.p. of $C_{10}H_{15}NO$ 130°) also by conversion of the fraction into dipentene[6]) (m.p. of tetrabromide 124 to 125°) its identity with d-α-*pinene* was established. The statements as to the optical rotation differ. Muir and Sugiura found it lævogyrate on one occasion, dextrogyrate on another, whereas Wallach found it inactive. In all probability, therefore, the pinene consists of a mixture of both optical isomers, in which one or the other predominates.

Fraction 174 to 178° yielded no nitrosylchloride. With the aid of hydrogen bromide Wallach succeeded in separating pure

[1]) As German oil of sage the oil distilled in Germany is understood in this case.

[2]) Berl. Berichte 35 (1902), 550.

[3]) Journ. Chem. Soc. 1877, I. 554; Jahresb. f. Chem. 1877, 427.

[4]) Philosoph. Magaz. and Journ. of Science V. 4 (1877), 336. — Pharmaceutical Journ. III. 8 (1877), 191, 994; Journ. Chem. Soc. 1877, II. 548; Jahresb. f. Chem. 1877, 957. — Chem. News 37 (1878), 211; Journ. Chem. Soc. 33 (1878), 292; Jahresb. f. Chem. 1878, 980. — Journ. Chem. Soc. 37 (1880), 678; Chem. News 41 (1880), 223; Jahresb. f. Chem. 1880, 1080.

[5]) Liebig's Annalen 252 (1889), 103.

[6]) *Ibidem* 227 (1885), 289.

cineol[1]). Fraction 198 to 203° was named "salviol" by Muir and Sugiura who first assigned to this substance the formula $C_{10}H_{16}O$, later $C_{10}H_{18}O$. Semmler at first declared this "salviol", which constitutes 50 p.c. of the oil, as identical with thujone or tanacetone[2]), but later expressed his doubts as to the correctness of this assumption[3]). By comparing the physical properties of the substance from the oils of sage, thuja, tansy and wormwood, after purification through the bisulphite addition products, Schimmel & Co.[4]) arrived at the conviction that they are all identical. Finally Wallach[5]) obtained the same derivatives, no matter whether he started from thujone, tanacetone, salvone or absinthol.

As proven later by Wallach[6]), sage oil contains d-*β-thujone* (m. p. of semicarbazone 174°) side by side with l-*α-thujone* (m. p. of semicarbazone 186°).

After oxidation of sage oil F. Rochleder[7]) had obtained camphor which was either contained originally in the oil or which was obtained upon oxidation of borneol. The higher fractions of the oil examined by Sugiura and Muir separated crystals upon cooling. These resembled camphor but did not correspond to it in all particulars. In order to decide whether camphor is contained in oil of sage, Schimmel & Co.[8]) fractionated an oil distilled from Dalmatian herb and exposed the fractions which, according to their boiling temperature ought to contain any camphor present, to the temperature of a freezing mixture without, however, being able to separate anything solid. Inasmuch as acetylation of fraction 205 to 215° revealed the presence of an alcohol (about 8 p.c. computed as $C_{10}H_{18}O$) part of it was treated with benzoyl chloride. After separation and saponification of the benzoic ester, a substance with all the properties of *borneol* (m.p. 204°; $α_D$ in 10 p.c. alcoholic solution $+ 0°23'$) was obtained.

[1]) Liebig's Annalen 252 (1889), 103.
[2]) Berl. Berichte 25 (1892), 3350.
[3]) *Ibidem* 27 (1894), 895.
[4]) Report of Schimmel & Co. October 1894, 56.
[5]) Liebig's Annalen 286 (1895), 93.
[6]) *Ibidem* 336 (1904), 270.
[7]) *Ibidem* 44 (1842), 4.
[8]) Report of Schimmel & Co. October 1895, 42.

Hence the borneol of oil of sage is slightly dextrogyrate. According to this investigation camphor could not be detected in sage oil.

In a later investigation, however, Schimmel & Co.[1]) succeeded in finding d-*camphor* (m. p. of oxime 118°). With borneol it is contained principally in the oil obtained upon cohobation of the aqueous distillate.

According to Muir[2]) English oil of sage contains much *cedrene*, b. p. 260°, little terpene and only traces of oxygenated constituents (?).

781. Oil of Salvia triloba.

A Syrian oil of sage having been sent from Jaffa to Schimmel & Co.[3]), its botanical origin was established by Dr. A. Ginzberger, of the Botanical Institute of Vienna, as *Salvia triloba*, L. It had the following constants: $d_{15°}$ 0.9116; α_{D} — 3° 28'; E.V. 10.3 corresponding to 3.6 p.c. of bornyl acetate; soluble in 15 to 16 vol. of 70 p.c. alcohol and in 1 vol. and more of 80 p.c. alcohol.

An investigation conducted later[4]) revealed the presence of *cineol* (m.p. of iodol compound 113 to 114°) and small amounts of l-*camphor* (m.p. of semicarbazone 235 to 236°). The highest boiling fraction yielded a semicarbazone which was treated with methyl alcohol. The residue contained camphor semicarbazone. Upon evaporation of the methylalcoholic solution, a semicarbazone remained which, after another purification melted at 162°. Upon hydrolysis with sulphuric acid the product had the odor of *thujone*.

782. Oil of Salvia cypria.

Salvia cypria, Ung. et Kotschy, which grows on the Island of Cyprus, yields a pale yellow oil[5]) the odor of which reminds of camphor and camphor oil. In connection with two oils the following constants were observed: $d_{15°}$ 0.9263 and 0.925; $\alpha_{D20°}$ — 6° 31' and — 22° 23'; S.V. 13.9 and 8; S.V. after acetylation 38.9 and 36; soluble in 0.8 and 1 vol. respectively of 80 p.c. alcohol. The oil differs from ordinary oil of sage by its lævo-

[1]) Report of Schimmel & Co. October 1907, 83.

[2]) *Loc. cit.*

[3]) Report of Schimmel & Co. October 1907, 81.

[4]) *Ibidem* April 1915, 40.

[5]) Bull. Imp. Inst. 11 (1913), 429

rotation. It contains about 75 p.c. *cineol* (resorcinol method) and a little *camphor*.

One of these oils agrees fairly well with an oil which Schimmel & Co.[1] had obtained several years previously from the Imperial Institute and which also had been produced in Cyprus. It was pale yellow, of characteristic odor and had the following constants: $d_{15°}$ 0.9263; α_D — 6°15'; $n_{D20°}$ 1.46664; A.V. 0; E.V. 6.4; E.V. after acetylation 36.0; soluble in 1 vol. of 80 p.c. alcohol yielding an opalescent solution; the solution in 90 p.c. alcohol, although clear at first, became opalescent upon dilution.

Identical with this oil is possibly one that was supposed to have been obtained from the large-flowering sage and which was examined by O. Wallach[2]. $d_{15°}$ 0.9084; α_D — 10.06°. It contained not a trace of thujone, but l-*α-pinene* (m. p. of nitroso-pinene 132°), *cineol* (hydrogen bromide addition product) and l-*camphor* (m. p. of semicarbazone 236°). Fraction 160 to 175 yielded with nitrous acid a crystalline substance that melted at 85 to 86°, but which did not behave like one of the known phellandrene nitrites.

Several lævogyrate oils of sage of unknown botanical origin have been described in literature. Inasmuch as their constants agree fairly well with those of *S. cypria* and *S. triloba,* the possibility is not excluded that they may have been obtained from either the one or the other of these species: —

From Syria:

$d_{15°}$	α_D	$n_{D20°}$	A.V.	E.V.	E.V. after acet.	Soluble in
0.9175[3]	— 9°35'	1.46734	—	7.3	—	1 vol. and more of 80 p.c. alcohol.
0.9283[4]	— 4°	—	1.5	9.8.	—	not soluble in 10 vol. of 80 p.c. alcohol. Apparently resinified.
0.9843[5]	— 6'8'	—	—	—	—	1.5 vol. and more of 70 p.c. alcohol. 1 vol. and more of 80 p.c. alcohol.

From Corfou:

0.9153[6]	— 15°14'	1.46882	0.5	9.0	—	Sol. in abt. 25 vol. of 70 p.c. alcohol, in 1.3 vol. and more of 80 p.c. alcohol.
0.9132[6]	— 15°5'	1.46832	0.5	10.6	—	

[1] Report of Schimmel & Co. October 1910, 112.
[2] Nachr. K. Ges. Wiss. Göttingen 1905, fascicle 1, p. 1. Meeting of February 11, 1905.
[3] Report of Schimmel & Co. October 1905, 62.
[4] Observation made in the laboratory of Schimmel & Co.
[5] Berichte von Roure-Bertrand Fils April 1911, 25.
[6] Report of Schimmel & Co. April 1909, 82.

783. Muscatel Sage Oil.

Origin and Production. Muscatel sage, *Salvia Sclarea,* L. is indigenous to northern Africa and southern Europe. Formerly it was cultivated here and there in vineyards from which it has spread. At the present time the plant is cultivated in Germany (Miltitz)[1]) and in southern France (Hérault, Gard, Vaucluse, Var, Alpes-Maritimes)[2]) for the purpose of distilling the oil. The inflorescences are distilled with and without the leaves. The yield varies considerably depending upon whether many or few leaves are used, or whether the parts of the plants are fresh, wilted or dry at the time of destillation. Computed with reference to the fresh material, the yield varies between 0.03 and 0.14 p.c., and computed with reference to the dry herb between 0.2 and 1 p.c. In France[2]) the fresh flowers yield 0.05 to 0.08 p.c., rarely 0.1 p.c. of oil.

Properties. The odor is agreeably lavender-like and after evaporation of the more volatile portions, very much like ambra. Like the yields, so the properties vary within wide limits.

The following properties have been observed in connection with *German oil:* $d_{15°}$ 0.910 to 0.960; α_D lævogyrate up to -45, in individual instances slightly dextrogyrate; $n_{D20°}$ 1.477 to 1.504; A. V. 1 to 17; E. V. 18 to 155 = 6.3 to 54.25 p.c. ester computed as linalyl acetate. Of 90 p.c. alcohol 1.5 vol. are required to effect solution. However, the addition of more alcohol causes opalescence and even turbidity as a result of paraffin separation.

French oil: $d_{15°}$ 0.896 to 0.930[3]); α_D -11 to $-63°$[3]); $n_{D20°}$ 1.464 to 1.474; A. V. up to 1; E. V. 110 to 206[4]) = 38 to 73 p.c. of linalyl acetate; soluble in 1 to 2 vol. of 80 p.c. alcohol, more solvent causes turbidity. Of 90 p.c. alcohol up to 0.5 vol. suffice to effect solution, the addition of more solvent again causes opalescence and turbidity with most oils.

Composition. After saponification of the oil, Roure-Bertrand Fils[5]) obtained considerable amounts of *linalool* which was

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[1]) Bericht von Schimmel & Co. April 1889, 44; Report of Schimmel & Co. October 1894, 38.

[2]) Parfum. moderne 5 (1912), 91.

[3]) Berichte von Roure-Bertrand Fils April 1906, 40.

[4]) Parfum. moderne 5 (1912), 93.

[5]) Berichte von Roure-Bertrand Fils April 1908, 10.

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characterized by its phenyl urethane melting at 65°. Although the acid in the saponification lye was not identified, the lavender-like odor of the oil renders the presence of the linalool as acetate probable, an occurrence previously alluded to[1]). In addition to the *ester* the oil contains *free linalool*[2]).

784. Oil of Ramona stachyoides.

Black sage, or *Ramona stachyoides,* (Benth.) Briquet (*Audibertia stachyoides,* Benth.; *Salvia mellifera,* Greene) is a shrub-like labiate that grows in southern California. From the fresh, flowering plants F. Rabak[3]) obtained 0.75 p.c. of a colorless oil that had an odor of camphor and revealed the following properties: $d_{21°}$ 0.9144; $\alpha_{1)}$ + 30.2°; $n_{D24°}$ 1.4682; A. V. 2; E. V. 2.5; E. V. after acetylation 27.1; soluble in 1.5 vol. of 70 p.c. alcohol, the addition of more than $3^1/_2$ vol. caused turbidity of the solution. At — 15° there separated 11.3 p.c. of d-*camphor* (m. p. 174 to 175°; m. p. of semicarbazone 232 to 233°). Of free acids it contained small amounts of *formic acid,* of combined acids *acetic acid* and possibly a trace of formic acid. Of other constituents the oil contained 22.5 p.c. of *cineol* (m. p. of iodol compound 111 to 112°), possibly also pinene, thujone and borneol. The total camphor content amounted to about 40 p.c.

Later an oil was examined by C. E. Burke and C. C. Scalione[4]) which had been distilled with a yield of about 0.9 p.c. from leaves and twigs collected in February. In the course of transportation the material had dried somewhat. It had the following properties: $d_{15°}$ 0.8979; $\alpha_{1)}$ + 24.4°; $n_{1)}$ 1.4729; A. V. 2.2; E. V. 1.6; insoluble in 70 p.c. alcohol. Exposed to low temperature no solid separated, thus differing from the oil of Rabak which at — 15° separated 11.3 p.c. of camphor. The following constituents were identified: 6 p.c. *α-pinene* (m. p. of hydrochloride 131°), 30 p.c. *cineol* (phosphoric acid method, identified by means of its iodol compound), 25 p.c. inactive *terpenes,* 8 p.c. *thujone* (b. p. 200°; d 0.917; α 25.9°; m. p. of tribromide 122°), 25 p.c.

[1]) Report of Schimmel & Co. October 1894, 38.

[2]) Observation made in the laboratory of Schimmel & Co.

[3]) U. S. Dep. of Agriculture, Bureau of Plant Industry, Bull. No. 235, p. 14; Report of Schimmel & Co. April 1912, 107.

[4]) Journ. Ind. Eng. Chemistry 6 (1914), 804.

camphor and 5 p.c. resinified material. The inactive terpenes possibly consist of dipentene and terpinene. Traces of a solid bromide indicate the presence of the first, whereas a brown precipitate, which resulted upon shaking with Beckmann's chromic acid mixture, indicated terpinene [1]).

The oil examined by Rabak contained more high-boiling constituents, which fact is probably due to the circumstance that the distilled plant material had been collected later in the season.

785. Oil of Meriandra dianthera.

From the Government of the Italian colony Eritrea Schimmel & Co. [2]) obtained two distillates supposed to be sage oils. They were light brown in color and had an odor, which, while it reminded of sage, was quite distinct therefrom. Moreover, the oils had a higher specific gravity than oil of sage and differed also in being lævogyrate. Inasmuch as a specimen of the plant distilled was sent with the oils it was possible to have the botanical source determined. Dr. Giessler, custodian in the Botanical Institute of the University of Leipzig, established that the plant does not belong even to the genus *Salvia*, but is identical with *Meriandra dianthera*, Briq. (*M. benghalensis,* Benth.). The leaves of the labiate are used in domestic medicine in the same way as are the leaves of sage. Distillation of the leaves yielded 1.5 p.c. of a light brown oil, the odor of which suggests both sage and rosemary; $d_{15°}$ 0.9513; $\alpha_D - 2°5'$; $n_{D20°}$ 1.47490; A. V. 3.7; E. V. 14.8; soluble in 2 vol. and more of 70 p.c. alcohol. Exposed to a freezing mixture the oil congealed to a butyraceous mass due to camphor.

The two oils distilled in Eritrea had the following properties:
1. $d_{15°}$ 0.9464; $\alpha_D - 0°30'$; $n_{D20°}$ 1.47176; A. V. 1.0; E. V. 11.8; soluble in 2 vol. and more of 70 p.c. alcohol.
2. $d_{15°}$ 0.9526; $\alpha_D - 1°$; $n_{D20°}$ 1.47548; A. V. 5.6; E. V. 9.3; soluble in 1.8 vol. and more of 70 p.c. alcohol.

Neither of the oils had its complete camphor content. In the preparation of oil No. 1 part of the camphor separated in the condenser. In the case of oil No. 2 part of the camphor

[1]) Comp. von Baeyer, Berl. Berichte 27 (1894), 815.
[2]) Report of Schimmel & Co. October 1911, 107.

had been removed by freezing. Samples of *camphor* from both oils were sent from Eritrea and were identified by the m. p. (176°) and the oxime (m. p. 118.5°). An optical examination revealed the camphor to be the dextrogyrate modification.

786. Oil of Monarda punctata.

Origin and Production. In North America the perennial labiate *Monarda punctata,* L. is known as horsemint. Distilled in the fresh condition the herb yields up to 1 p.c.; in the dry condition up to about 3 p.c. of volatile oil. This has a yellowish-red or brownish color and a pungent, thyme-like and minty odor. d 0.930 to 0.940; α_D mostly inactive or slightly dextrogyrate. Upon prolonged standing the oil separates crusts of heavy crystals of thymol, of which phenol it contains about 60 p.c.[1]).

Composition. Thymol was found in monarda oil by A. E. Arppe[2]) in 1846. The thymol content is so large that for a short period the oil was used for the commercial production of this phenol[3]). More recently its cultivation for this purpose has been recommended in the United States[4]). According to the investigation of H. J. M. Schröter[5]) the oil was reported to contain 50 p.c. of a lævogyrate hydrocarbon boiling between 170 and 173°, 25 p.c. of a dextrogyrate (!) non-crystallizable thymol, and a substance $C_{10}H_{18}O$ (?) boiling between 240 and 250°. These statements, that do not inspire confidence, make it seem doubtful as to whether Schroeter really had oil of *Monarda punctata* under investigation.

In order to leave no doubt as to the botanical source, W. R. Schumann and E. Kremers[6]) had the plant material examined by a botanical authority. The oil was distilled from fresh wild growing plants, growing not far from Madison, Wis., and yielded 61 p.c. of thymol (determined according to the method of Kremers and Schreiner described in vol. I, p. 594). The bulk of the non-

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[1]) Comp. N. Wakeman, The Monardas. Madison 1911. Bulletin of the University of Wisconsin No. 448.

[2]) Liebig's Annalen 58 (1846), 41.

[3]) Comp. also Bericht von Schimmel & Co. October 1885, 20.

[4]) F. Rabak, Americ. Perfumer 5 (1910), 220.

[5]) Americ. Journ. Pharm. 60 (1888), 113.

[6]) Pharm. Review 14 (1896), 223.

phenol portion of the oil consisted of *cymene* $C_{10}H_{14}$, which was identified by means of the hydroxy*iso*propyl benzoic acid melting at 155 to 156°. Fraction 186 to 202° contained oxygen and consisted apparently of linalool.

According to more recent investigations by W. E. Hendricks and E. Kremers[1]) thymol is accompanied at times by a second phenol which does not congeal when cooled, presumably *carvacrol*. In addition the presence of traces of d-*limonene* was demonstrated by means of limonene nitrolbenzylaminc melting at 94°.

787. Oil of Monarda citriodora.

Origin and Production. *Monarda citriodora*, Cerv., known in North America as lemon mint, occurs from Illinois westward to Nebraska and southward to Texas[2]).

From the dry, flowering herb I. W. Brandel[3]) obtained about 1 p.c. of oil.

Properties. It is a reddish oil with a lemon-like odor. $d_{20°}$ 0.9437[3]) to 0.9603[4]). Phenol content 65 to 80 p.c.; aldehyde content 1.2 to 4 p.c.

Composition[3]). The bulk of the oil consists of *carvacrol* (m. p. of benzoyl derivative of nitrosocarvacrol 110°). It possibly also contains traces of thymol. The highest boiling phenol portions contain *thymohydroquinone* (m. p. 140°). Judging from its odor, the aldehyde appears to consist wholly or at least in large part of *citral*. *Cymene* may also be present. The melting point of the acid obtained upon oxidation of the cymene was 124° in place of 156°.

788. Oil of Monarda didyma.

Origin and Production. Flückiger[5]) alludes to the oil of *Monarda didyma*, L., a native of North America, in the following words: "In 1796 the apothecary Brunn, of Güstrow, observed a deposit

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[1]) Pharm. Archives **2** (1899), 73.

[2]) N. Wakeman, *loc. cit.* p. 8.

[3]) Pharm. Review **22** (1904), 153.

[4]) C. Lefebvre and N. Wakeman, Midland Drugg. and Pharm. Review **44** (1910), 526.

[5]) Arch. der Pharm. **212** (1878), 488.

in the oil of *Monarda didyma*, L. (presumably thymol) which, as
it would appear, was imported from America."

A more recent investigation carried out by I. W. Brandel[1]),
however, showed that the oil contains neither thymol nor
carvacrol. Hence it is to be assumed that the earlier investi-
gators had some other monarda oil in hand.

The dried herb yielded 0.03 p. c. of oil upon distillation[1]).
According to Schimmel & Co.[2]) the half-dried herb yielded
0.04 p. c., the stems and leaves 0.096 p. c.[3]), the half-wilted
flowers 0.26 to 0.32 p. c.[3])[4]) of oil.

Properties. The oil is pale yellow to reddish-brown and
has a sweet balsamic odor, lavender-like, reminding of linalool
and its ester with a suspicion of ambra.

No.	Distilled from	$d_{15°}$	α_D	$n_{D20°}$	A.V.	E.V.	Soluble in
1.	dry herb[1])	0.902 at 20°	− 10°	—	—		1.5 to 2 vol. of 70 p. c. alcohol, the addition of more causes turbidity because of the separation of paraffin
2.	half-dried herb[2])	0.8786	−24°36′	1.46763	—	—	
3.	almost dry stems and leaves[2])	0.8855	−32°38′	1.46892	5.5	20.4	2 vol. and more of 70 p c. alcohol, more causes turbidity.
4.	half-wilted flowers[2])	0.8665	− 7°30′	1.46892	2.4	4.4	20 vol and more of 70 p c. alcohol with separation of paraffin.
5.	")	0.8740	15°45′	1.46743	4.6	5.6	3 vol. and more of 70 p. c. alcohol, the addition of 6 vol. causes turbidity.

789. Oil of Monarda fistulosa.

Origin and Yield. *Monarda fistulosa*, L., known in North
America as wild bergamot, yields upon distillation an oil similar
to that of *Monarda punctata*[5]).

The yield from fresh, flowering herb amounts to 0.3 to
1 p.c.[6]), for the most part 0.5 to 0.75 p.c.[7]), whereas the dry
floral leaves yielded 2.71 p.c.[8]).

[1]) Pharm. Review 21 (1903), 109.
[2]) Report of Schimmel & Co. October 1904, 97.
[3]) *Ibidem* November 1908, 86.
[4]) *Ibidem* October 1909, 80.
[5]) E. Kremers, Pharm. Rundsch. (New York) 13 (1895), 207. -- E. J. Melzner and E. Kremers, Pharm. Review 14 (1896), 198.
[6]) F. Rabak, Americ. Perfumer 5 (1910), 221.
[7]) N. Wakeman, *loc. cit.*
[8]) J. J. Beck and I. W. Brandel, Pharm. Review 21 (1903), 109.

Properties. The specific gravity of a number of oils which had been distilled from flowering plants in different stages of vegetation, from the months of June to September, lay between 0.916 and 0.941. Optical rotation slightly lævogyrate. The phenol (carvacrol) content fluctuates between 52 and 72 p.c. An oil distilled from the leaves deprived of stems was straw-yellow in color, $d_{20°}$ 0.9241, α_D — 0°9'. The oil distilled from the florets was red-brown, d 0.9586. It also contained carvacrol[1]).

Composition. In addition to little *limonene* (m. p. of nitrol-benzylamine 93°)[2]) the oil contains *cymene* (m. p. of hydroxy-*iso*propyl benzoic acid 156°) and *carvacrol* (67 p.c. determined with dilute lye). This substance was identified by conversion into dicarvacrol (m. p. 147 to 148°), carvacrol sulphonic acid (m. p. 58 to 59°), nitrosocarvacrol (m. p. 153 to 154°) and di-nitrocarvacrol (m. p. 117 to 119°). Another phenol is *thymo-hydroquinone* (m. p. 140°) small amounts of which were found by E. Kremers and I. W. Brandel. In addition *thymoquinone*[1]) is present. This is noteworthy since previously no quinone had been found in a volatile oil.

The simultaneous occurrence of these two substances admits of the supposition that *Monarda fistulosa* owes its color to these constituents, which possibly combine to form the highly pigmented quinhydrone.

Upon steam distillation of the phenols separated by means of acid from the alkaline solution, a red crystalline substance separated in the cooler. After purification by sublimation it melted at 256 to 266° and acted toward alkalis like alizarin[3]).

Later S. K. Suzuki[4]) showed that this red substance is no alizarin and finally N. Wakeman[5]) showed that the substance was *dihydroxythymoquinone* (green precipitate with lead acetate).

The alcohol contained in the oil presumably has the formula $C_{10}H_{17}OH$[6]). Jointly with N. Wakeman[7]), E. Kremers has

[1]) J. J. Beck and I. W. Brandel, Pharm. Review 21 (1903), 109.

[2]) W. E. Hendricks and E. Kremers, Pharmaceutical Archives 2 (1899), 76.

[3]) E. Kremers, Pharm. Rundsch. (New York) 13 (1895), 207, — E. J. Melzner and E. Kremers, Pharm. Review 14 (1896), 198.

[4]) Midland Drugg. and Pharm. Review 44 (1910), 342.

[5]) *Loc. cit.* p. 23.

[6]) I. W. Brandel and E. Kremers, Pharm. Review 19 (1901), 200.

[7]) *Ibidem* 26 (1908), 314, 329, 364.

conducted quantitative experiments as to the oxidase[1]) occurring in the leaves of *Monarda fistulosa*. This enzyme oxidizes the thymohydroquinone contained in the plant. It should be added that thymoquinone, dissolved in alcohol or limonene, is reduced to quinhydrone or, more correctly, thymohydroquinone.

790. Pennyroyal Oil.

Origin and Production. The oil of *Hedeoma pulegioides,* (L.) Pers., known in North America as pennyroyal, so closely resembles the European oil of *Mentha Pulegium*, L. that it frequently is substituted for the latter. Inasmuch as pennyroyal[2]) is distributed from the Atlantic States to the Rocky Mountains, and since the distillation can be conducted with simple apparatus, the oil is produced in a number of places. The bulk of the oil is said to be distilled in North Carolina[3]) and particularly in the southern and eastern part of Ohio[4]) and more recently also in Tennessee[5]). The primitive stills, the same type that is used in the distillation of sassafras and wintergreen oils, consist of a barrel supported on a pan and connected with a cooler supported in a trough. The entire outfit rests on a fireplace dug into the ground and provided with a chimney. The best yield, namely 0.6 to 1 p.c.[6]) is obtained from the fresh flowering herb. From every ton of fresh herb 10 to 12 lbs. of oil are obtained. Dry leaves yielded[7]) 3 p.c., dried stems and leaves only 1.3 p.c. of oil.

Properties. American pennyroyal oil is a light yellow liquid with a characteristic, minty yet sweetish odor and aromatic taste. $d_{15°}$ 0.925 to 0.940; $\alpha_D + 18$ to $+ 35°$. It is soluble in two and more parts of 70 p.c. alcohol. This property enables

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[1]) As to the oxidase comp. also F. Rabak, Pharm. Review 22 (1904), 190 and D. B. Swingle, *ibidem* 193.

[2]) The word "penny" in the designation pennyroyal is possibly a corruption of the word "pulliol", for in the old English literature this plant is named "pulliol" royal. Pharmaceutical Journ. III. 87 (1911), 652, 700.

[3]) T. C. Harris, Pharmaceutical Journ. III. 17 (1887), 672.

[4]) Kremers, Proceed. Americ. pharm. Ass. 35 (1887), 546. — J. F. Patton, Proceed. Pennsylv. pharm. Ass. 1890 and Proceed. Americ. pharm. Ass. 39 (1891), 548. — Jahresber. d. Pharm. 1890, 378.

[5]) Report of Schimmel & Co. October 1907, 68.

[6]) F. Rabak, Americ. Perfumer 5 (1910), 221.

[7]) Report of Schimmel & Co. October 1898, 29.

the detection of petroleum, turpentine oil and resin oil, recorded by E. Kremers[1]), also of other difficultly soluble volatile oils.

Composition. *Pulegone* must be regarded as the characteristic constituent of American pennyroyal oil. Its presence was demonstrated by C. J. Habhegger[2]) by the preparation of the pulegone oxime hydrate, $C_{10}H_{16}NOH \cdot H_2O$, melting at 147°, also by the benzoyl ester of this oxime melting at 141°. Concerning the amount of pulegone present only one observation is to be found in literature in addition to those recorded below. With the aid of neutral sodium sulphite H. E. Burgess[3]) found 16 p.c. of pulegone.

According to E. Kremers[4]) the oil contains two additional ketones, both having the formula $C_{10}H_{18}O$. The one, *hedeomol*, boils at 168 to 171° and is characterized by an oxime melting at 41 to 43°. The second, boiling at 206 to 209°, yields an oxime melting at 52° and is probably identical with *menthone*. In addition, Kremers found traces of *formic acid, acetic acid* and iso*heptoic acid*.

More recently the oil has been examined by M. Barrowcliff[5]). Of free acids *formic, butyric, octylic,* and *decylic acids* were found to be present. Upon shaking the oil with 5 p.c. caustic potassa solution he obtained a small amount of phenols that were not identified, also traces of *salicylic acid,* which probably were present in the oil as methyl ester. From the portion distilling above 120° (60 mm.) pulegone (24.1 p.c. of the oil) was separated by means of acid sulphite solution. It was identified by means of its semicarbazone melting at 171°. After the treatment with bisulphite, the oil was saponified, the resulting oil distilled under 60 mm. pressure, combined with the portions that had boiled below 120° (60 mm.) after treatment with soda and caustic potash, and the combined oil fractionated under ordinary pressure. In fraction 155 to 165° thus obtained small amounts of l-α-*pinene* were found (m. p. of nitrolbenzylamine 122°).

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[1]) Proceed. Americ. Pharm. Ass. 50 (1902), 979.

[2]) Americ. Journ. Pharm. 65 (1893), 417.

[3]) Analyst 29 (1904), 78.

[4]) Proceed. Americ. Pharm. Ass. 85 (1887), 546; Améric. Journ. Pharm. 59 (1887), 535. — Pharm. Rundsch. (New York) 9 (1891), 130.

[5]) Journ. Chem. Soc. 91 (1907), 875.

In fraction 165 to 170° *l-methyl-3-cyclohexanone* (8 p.c.) was shown to be present. After regeneration from its semicarbazone (m. p. 182 to 183°) it distilled at 167 to 168°. Apparently this is the first time that this ketone was observed in nature. The same fraction, also the next higher one from 170 to 180° contained small amounts of l-*limonene* and *dipentene* (tetrabromides).

After remaining traces of pulegone had been removed from fraction 212 to 217° it was used for the preparation of the semicarbazone. Two substances were obtained. The one proved to be the semicarbazone of l-*menthone* (m. p. 184 to 186°), the other that of d-*menthone* (m. p. 125 to 126°). The combined ketone constituted 50 p.c. of the oil. The *l*-menthone regenerated from the semicarbazone boiled at 207 to 208° (m. p. of oxime 58 to 59°); the *d*-menthone, regenerated in like manner, boiled at 209 to 210° (its oxime was oily). The latter menthone was found to be identical with the inverted menthone and, according to O. Aschan's nomenclature, is to be designated d-*iso*menthone. Fraction 300 to 310° contained a *sesquiterpene alcohol* (2 p.c.) from which a sesquiterpene with the following properties was obtained: $d_{20°}$ 0.8981; $\alpha_D + 1°4'$; $n_{D20°}$ 1.5001; b. p. 270 to 280°; mol. refr. 66.8. Of combined acids Barrowcliff found, in addition to the salicylic acid already mentioned, *formic, acetic, octoic* and *decoic acids,* also a non-volatile, *dibasic acid,* m. p. 83 to 85°, presumably of the formula $C_8H_{14}O_4$.

791. Oil of Balm.

Oleum Melissæ. — Melissenöl. · Essence de Melisse.

Origin. *Melissa officinalis,* L., a labiate, is indigenous to the countries north of the Mediterranean from Spain to the Caucasus. It is also cultivated in Europe and North America both as a decorative plant and for medicinal purposes.

Properties and Composition. Commercial oil of balm is no pure distillate of melissa. It is either lemon oil distilled over balm *(Oleum Melissæ citratum),* or citronella oil thus treated. At times it is nothing more or less than fractionated citronella oil. The yield of true oil of *Melissa officinalis,* L. is so minimal that the price of the oil would render it unmarketable.

An oil distilled by Schimmel & Co. from dry herb solidified at ordinary temperature and contained citral[1]) as was proven by means of Doebner's reaction. Later the fresh herb of two varieties of melissa[2]) was distilled by the same firm.

1. Fresh herb during the flowering stage: yield 0.014 p.c.; $d_{15°}$ 0.924; $\alpha_D + 0°30'$. The oil possessed a very pleasant odor of balm.

2. Fresh herb in full bloom: yield 0.104 p.c.; $d_{15°}$ 0.894; optically inactive. Its odor, which was less pleasant than that of the first oil, plainly revealed citral and citronellal.

The attempt to prove the presence of both aldehydes by means of Doebner's method yielded no definite results. The acids obtained from both oils began to melt at 208° and had completely liquified at 225°. Presumably they represented a mixture of the citral compound, which melts at 197 to 200°, with that of the citronellal derivative melting at 225°.

792. Oil of Satureia montana.

Origin. The oil of *Satureia montana*, L., which plant is known in the French Alps as *poivre d'âne*, has almost the same composition as the oil of *Satureia hortensis*, neither can it be distinguished from the latter by its odor.

Properties and Composition. From fresh cultivated herb Schimmel & Co.[3]) obtained upon distillation 0.18 p.c. of oil. $d_{15°}$ 0.939; $\alpha_D - 2°35'$; with 4.5 parts of 70 p.c. alcohol and with $1^1/_2$ parts of 80 p.c. alcohol it yielded a clear solution. It contained 65 p.c. phenol.

An oil examined by A. Haller[4]) had been distilled near Grasse from the herb of the wild plant growing in the Maritime Alps. $d_{17°}$ 0.9394[5]); $\alpha_D - 3°25'$. He found 35 to 40 p.c. *carvacrol*, also small amounts of a phenol boiling above 235°. The hydrocarbons of the oil passed over between 172 to 175° and 180 to 185° and seemed to be terpenes.

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[1]) Report of Schimmel & Co. October 1894, 38.

[2]) *Ibidem* October 1895, 65.

[3]) *Ibidem* October 1897, 59.

[4]) Compt. rend. 94 (1882), 132.

[5]) Haller's statement of the specific gravity as 0.7394 no doubt is due to a printer's error.

Two oils distilled in southern France by Schimmel & Co.[1]) from flowering herb were lemon-yellow and brownish-yellow in color respectively, and had an odor of thyme. Their other properties are herewith tabulated: —

	Yield	d_{15°	α_D	n_{D20°	
Distilled in Barrême	0.23 p.c.	0.908	$-1^\circ 42'$	1.49488	Sol. in 8 vol. and more of 80 p.c. alcohol.
Distilled in Sault . .	0.15 p.c.	0.9194	$-4^\circ 48'$		Sol. in 1.5 vol. and more of 80 p.c. alcohol.

Both oils contained *carvacrol*; the Barrême oil 27 p.c., that from Sault 32 p.c.

S. S. Pickles[2]) described an oil obtained from a variety of *Satureia montana*, L. which in its properties resembled that of *Satureia cuneifolia*. The dry herb from Trieste yielded 1.64 p.c. of a golden-yellow oil with a carvacrol-like odor and the following properties: d_{15° 0.9548; $\alpha_D - 1^\circ 3'$; soluble in 2.7 vol. of 70 p.c. alcohol. It contained 68.75 p.c. phenols, principally carvacrol.

793. Oil of Satureia hortensis.

Origin. *Satureia hortensis*, L., Ger. *Bohnen-* or *Pfefferkraut*, owes its odor and sharp taste to a volatile oil which is obtained by steam distillation. From fresh, flowering herb the yield is about 0.1 p.c.

Properties. The oil possesses the strongly aromatic odor of the plant and a pungent, sharp taste. The specific gravity of the oil distilled from fresh plants lies between 0.900 and 0.930; α_D (for two oils) $+0^\circ 4'$ and $-0^\circ 56'$. Phenol content 36 to 42 p.c. The oil is soluble in 2 parts of 80 p.c. alcohol but sometimes it requires 10 parts to yield a clear solution[3]). An oil examined by E. Jahns[4]) had been distilled from the dry herb; d 0.898; $\alpha_D - 0.62^\circ$; phenol content 30 p.c.

Composition. According to Jahns the phenol of this oil consists of *carvacrol* with traces of a second phenol which gives a blue color test with ferric chloride but which has not been more definitely determined.

[1]) Report of Schimmel & Co. April 1912, 116.
[2]) Proc. Chem. Soc. 27 (1911), 285. Comp. also Bull. Imp. Inst. 9 (1911), 388.
[3]) Report of Schimmel & Co. October 1897, 59.
[4]) Berl. Berichte 15 (1882), 816.

Of the hydrocarbons, a part (about $^1/_3$) distills between 173 and 175° and consists of *cymene* (cymene sulphonate of barium). The remaining portion (about $^2/_3$) distills between 178 and 180° (d 0.855; $\alpha_D - 0.2°$) and is a terpene as shown by elementary analysis.

794. Oil of Satureia cuneifolia.

Several oils distilled by Dr. Giaconi in Trieste, Dalmatia, from the labiate *Satureia cuneifolia,* Tenore, have been examined by Schimmel & Co.[1]). The color of these oils was brownish-yellow and their odor thyme-like. In other respects they revealed the following properties: —

No.	$d_{15°}$	α_D	$n_{D20°}$	Phenols	soluble in
1.	0.9182	4° 45'	1.49816	28 p.c.	1.2 & m. vol. of 80 p.c. alcohol.
2.	0.9190	− 5° 15'	1.49824	34 p.c.	1.1 & m. vol. of 80 p.c. alcohol.
3.	0.9444	− 2° 15'	1.50528	59 p.c.	2.5 & m. vol. of 70 p.c. alcohol.
4.	0.9440	− 1° 50'	1.50556	59 p.c.	2.7 & m. vol. of 70 p.c. alcohol.

Oils 1 and 2 did not dissolve in 10 vol. of 70 p.c. alcohol, for 3 and 4 about 1 vol. of 80 p.c. alcohol was required. The phenols consisted of *carvacrol,* the non-phenols had a distinct odor of *cymene* for the identification of which, however, the amount of oil was insufficient.

795. Oil of Satureia Thymbra.

Satureia Thymbra, L. which the ancient Greeks dedicated to Priapus, is used quite generally in Spain as a spice and has the reputation of a powerful stimulant and disinfectant. It owes these properties to its volatile oil. Such an oil obtained from Spain has been examined by Schimmel & Co.[2]). After removal of the *thymol* (about 19 p.c.) the oil was fractionated. The fraction distilling about 160° consisted of *α-pinene* (m.p. of nitrolbenzylamine 121°). At 175° *cymene* passed over and in the following fraction small amounts of *dipentene*. After saponification of the portion distilling above 200° borneol and acetic acid were obtained which are contained in the original oil as *bornyl acetate.* Hence the oil closely resembles oil of thyme as to composition.

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[1]) Report of Schimmel & Co. October 1911, 109.
[2]) Bericht von Schimmel & Co. October 1889, 55.

796. Oil of Field-balm.

Origin. From the fresh, flowering herb of *Satureia Cala-mintha*, (L.) Scheele, subspec. *silvatica*. Briq., var. *silvatia*, Briq. (*Melissa Calamintha*, L.), Ger. *Bergmelisse*, which is distributed throughout central Europe, Schimmel & Co.[1]) obtained at two different times a pleasantly aromatic oil.

Properties. $d_{15°}$ 0.8759 to 0.8771; α_D —16° 57' to —28°12'; $n_{D20°}$ 1.49110 to 1.49507; A. V. 0; E. V. 4.5 to 8.3; E. V. after acetylation (1 determination) 38.95; does not yield a clear solution with 10 vol. of 90 p.c. alcohol.

797. Oil of Calamintha Nepeta.

Origin. The labiate *Satureia Calamintha*, (L.) Scheele, sub-spec. *Nepeta*, Briq., var. *Nepeta*, Briq. (*Melissa Nepeta*, L.; *Cala-mintha parviflora*, Lam.; *C. trichotoma*, Mœnch.; *C. Nepeta*, Savi; *C. obliqua*, Host, &c.), the pulegium-like mountain mint, grows wild in the mountains of southern Europe, and is known in sou-thern France as *Marjolaine*[2]). It was formerly known in medicine as *Herba Calaminthæ vel Calaminthæ montanæ*.

Properties. An oil of French origin examined by Schimmel & Co.[3]) was of light, greenish-yellow color and had a minty odor: $d_{15°}$ 0.9271; α_D + 6° 49'; E. V. 13.0; soluble in 2.7 vol. and more of 70 p.c. alcohol.

Two oils distilled in Dalmatia[4]) had a minty odor and the following properties: $d_{15°}$ 0.9305 and 0.9395; α_D + 2° 50' and + 6° 28'; $n_{D20°}$ 1.48441 and 1.48920; A. V. 0.9; E. V. 5.4 and 14.6; soluble in 2 to 2.5 vol. of 70 p.c. alcohol. The pulegone assay of one of the oils with neutral sodium sulphite revealed a content of about 45 p.c.

An oil distilled in Sicily with a yield of 0.1426 p.c. had an odor that reminded of pulegium[5]) oil as did the preceding ones.

[1]) Report of Schimmel & Co. April 1901, 59; October 1905, 34.

[2]) Concerning the French designation *Marjolaine*, which is applied to *Majorana hortensis* as also to *Origanum vulgare* and *Calamintha Nepeta* comp. E. M. Holmes, Perfum. Record 3 (1912), 322.

[3]) Report of Schimmel & Co. October 1906, 14.

[4]) *Ibidem* October 1911, 24.

[5]) Berichte von Roure-Bertrand Fils October 1912, 73.

It revealed the following constants: d_{15° 0.9249; $\alpha_D + 17^\circ 48'$; A. V. 1.4; S. V. 12.6; E. V. after acetylation 48.5; soluble in 3 vol. of 70 p.c. alcohol, 2 vol. of 75 p.c. alcohol and 0.5 vol. of 80 p.c. alcohol. The addition of more of the 70 to 75 p.c. alcohol causes the solution to become opalescent to turbid. A pulegone assay with neutral sulphite revealed 20 p.c. Besides *pulegone* the oil probably contains *menthone*. This was indicated by the fact that the E. V. of the reduced and subsequently acetylated oil was 190.4, hence much higher than that of the original oil. In consequence of the formation of *l*-menthol from pulegone and menthone, the reduced oil revealed lævorotation ($\alpha_D -18^\circ$).

Another oil was examined by Wright, Layman & Umney[1]): d 0.922; $\alpha_D + 14^\circ$; ester content 4.2 p.c.; total alcohol content, computed as menthol, 18.2 p.c.; ketone content 10.8 p.c., presumably pulegone.

Composition. The lowest boiling fractions contain small amounts of l-*α-pinene* (hydrochloride, nitrosochloride[2])). The characteristic constituents are *pulegone* (m.p. of semicarbazone 172°[3])) and l-*menthone* (m.p. of semicarbazone 184°; m.p. of oxime 59°). The ketone named calaminthone by Genvresse and Chablay is not a chemical unit but a mixture of pulegone and menthone.

798. Oil of Satureia macrostema.

The oil of the shrub-like *Satureia macrostema*, (Benth.) Briq. (*Calamintha macrostema*, Benth.), indigenous to Mexico, has been described by Schimmel & Co.[4]). It is light yellow in color and has a mint-like odor. d_{15° 0.9182; $\alpha_D + 6^\circ 51'$; n_{D20° 1.46852; A. V. 15.6; E. V. 10.3; E. V. after acetylation 37.9. The oil was soluble in all proportions in 90 p.c. alcohol, also in 3 vol. of 70 p.c. alcohol and in 1.2 vol. of 80 p.c. alcohol. Both 70 and 80 p.c. alcohol, however, cause opalescence upon the addition of more solvent. The odor indicates the presence of pulegone.

[1]) Perfum. Record 3 (1912), 324.
[2]) P. Genvresse and E. Chablay, Compt. rend. 136 (1903), 387.
[3]) Report of Schimmel & Co. October 1906, 14.
[4]) *Ibidem* April 1909, 97.

799. Oil of Micromeria Chamissonis.

The perennial labiate *Micromeria Chamissonis,* Greene (*M. Douglasii,* Benth.), which occurs along the western coast of the United States and is there known as *Yerba Buena,* has been examined by F. B. Power and A. H. Salway[1].

Upon distillation with water vapor the air-dried herb yielded 0.16 p. c. of volatile oil. A semi-solid substance that passed over toward the end of the distillation, after drying on porous plate, revealed itself as *palmitic acid* (m. p. 61.5°). The slightly yellowish-brown oil with an agreeably aromatic, somewhat peppermint-like odor (d_{20}. 0.9244; α_D — 22° 48′) was not completely soluble in 10 vol. of 70 p. c. alcohol and gave no color reaction with ferric chloride.

Steam distillation of the alcoholic extract of the plants also yielded about 0.5 p. c. of a volatile oil resembling the previously described one as to appearance and odor. d_{15}. 0.9450; α_D — 26°44′. Contrasted with the oil obtained directly from the herb it was readily soluble in 70 p. c. alcohol. For the most part it distilled between 120 and 140° under 25 mm. pressure. The aqueous distillate contained *formic, acetic* and *butyric acids.*

800. Oil of Micromeria japonica.

According to Y. Murayama[2] the air-dried herb of *Micromeria japonica,* Miq. contains 0.7 p. c. of a yellow oil with a characteristic odor of peppermint. Fractional distillation yielded l-*menthone* which was characterized by boiling point, elementary analysis and preparation of its oxime. Menthol may also be a constituent of the oil.

801. Oil of Thymbra spicata.

The shrubby labiate *Thymbra spicata,* L. resembles thyme and is indigenous to Greece and Asia Minor. Herb from Smyrna was distilled by Schimmel & Co.[3]. It yielded 1.5 p. c. of a yellow oil with an odor of thyme and origanum. Its *carvacrol*

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[1] Journ. Americ. Chem. Soc. 30 (1908), 251.

[2] Journ. Pharm. Soc. of Japan 1911, 783. Through Zeitschr. d. allg. österr. Apoth. Ver. 50 (1912), 48.

[3] Report of Schimmel & Co. October 1910, 147.

content approximated 66 p.c. It had the following constants: d_{15} 0.9460; α_D + 0; $n_{D20°}$ 1.50675; soluble in 3.5 vol. of 70 p.c. alcohol.

802. Oil of Amaracus Dictamnus.

An oil designated *Essence de Dictame blanc ou Calament,* which had been distilled in Oran, Algiers, has been described by Schimmel & Co.[1]). It was probably derived from *Amaracus Dictamnus,* (L.) Benth. *(Origanum Dictamnus,* L., Ger. *Diptam-Doste)* and in its properties resembled the oils of *Calamintha Nepeta* and *Pulegium.*

The oil is of a yellow color and has a strong odor of pulegone. $d_{15°}$ 0.9331; α_D + 3°; soluble in 2.7 vol. of 70 p.c. alcohol with slight opalescence which was increased upon the addition of more solvent, until turbidity resulted with the increase to 14 vol. The oil contained about 85 p.c. of *pulegone* with an angle of rotation of + 20° 10′. The ketone had been separated by means of sodium sulphite solution.

Another sample of oil showed similar properties: d_{15} 0.9349; α_D + 6° 0′; A.V. 2.3; E.V. 20.9; E.V. after acetylation 80.0; yields a turbid solution with 2.3 vol. and more of 70 p.c. alcohol, which becomes opalescent upon the addition of more solvent. With the aid of sodium sulphite solution 66 p.c. of pulegone could be removed. The oil deprived of pulegone showed $d_{15°}$ 0.9201; α_D — 19° 16′ and had an odor reminding of menthol and borneol.

803. Oil of Hyssop.

Oleum Hyssopii. — Ysopöl. — Essence d'Hysope.

Origin. *Hyssopus officinalis,* L. which is indigenous to the Mediterranean countries and central Asia, grows wild in the hills of the Dauphiné and on the plains of the Provence[2]). In Germany (Miltitz) and southern France it is cultivated for the distillation of oil. Fresh to wilted herb yields 0.07 to 0.29 p.c. upon distillation, dry herb 0.3 to 0.9 p.c. of volatile oil.

Properties. It is a pleasantly aromatic liquid with a somewhat sweetish odor. $d_{15°}$ 0.927 to 0.945; α_D — 12 to — 25°; $n_{D20°}$ 1.473 to 1.486; A.V. up to 2; E.V. 3 to 15; E.V. after

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[1]) Report of Schimmel & Co. October 1906, 84.

[2]) H. Blin, Parfum. moderne 3 (1910), 134.

acetylation 37 to 47. Soluble in 0.5 to 8 vol. of 80 p. c. alcohol, in some instances turbidity (paraffin?) results at once or upon the addition of more solvent. French oils frequently are soluble in 4 to 6 vol. of 70 p. c. alcohol.

Very different were the properties observed by P. Jcancard and C. Satie[1]) in connection with two oils distilled in Cannes from fresh, flowering herb, presumably from a special variety[2]).

Distillate of 1903: $d_{15°}$ 0.9252; $\alpha_D + 1°$; A.V. 0.8; E.V. 9.2; E.V. after acetylation 70.0.

Distillate of 1908: $d_{15°}$ 0.9262; $\alpha_D - 2°6'$; A.V. 0.8; E.V. 11.9; E.V. after acetylation 51.1.

The pure French commercial oils, however, fluctuate in their properties between the limits given above. Frequently adulterated French oils are met with. Thus, in one instance, the specific gravity was 0.95 and the angle of rotation $+$ (!) 45°. This oil, as well as others, had a decided odor of fenchone, hence it was supposed that they consisted chiefly of the lower fractions of fennel oil. Specifically light oils with low angle of rotation are to be suspected of adulteration with oil of spike which has been observed repeatedly.

Composition. In 1842 Stenhouse[3]) analyzed fractions 160°, 167 and 180° but communicated nothing else that was noteworthy. In 1902 Genvresse and Verrier[4]) mention cineol and a tertiary alcohol $C_{10}H_{18}O$, b.p. 210 to 213° under 740 mm. pressure, as constituents, but reveal nothing more about the second substance. A more careful investigation of the oil, conducted with authentic material, was desirable, for nothing was known as to the origin of the hitherto examined oils, neither was there any criterion as to their possible adulteration. Such an investigation was made by E. Gildemeister and H. Köhler[5]) in connection with an oil distilled by themselves.

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[1]) Americ. Perfumer 4 (1909), 84.

[2]) Concerning the numerous varieties of *Hyssopus officinalis* see J. Briquet, in Engler-Prantl, *Die natürlichen Pflanzenfamilien*. Leipzig, IV. *Teil*, Abt. 3a, p. 306.

[3]) Liebig's Annalen 44 (1842), 310. — Journ. f. prakt. Chem. 27 (1842), 255.

[4]) Bull. Soc. chim. III. 27 (1902), 829.

[5]) *Wallach-Festschrift*, Göttingen 1909, p. 414. — Report of Schimmel & Co. April 1908, 57; October 1909, 69.

In the lowest boiling fraction (about 14 p. c.) β-*pinene* (m. p. of nopinic acid 126 to 127°) was identified. This is the first instance in which this hydrocarbon has been isolated in larger amount and relatively pure state from a volatile oil.
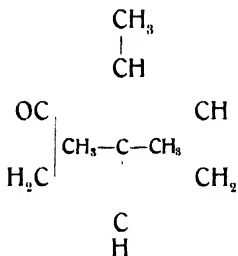
Almost one-half of the total oil consists of l-*pinocamphone*, $C_{10}H_{16}O$, a ketone heretofore unknown as a constituent of volatile oils. Its constitution finds expression in the accompanying structural formula.

Previously this compound had been obtained synthetically only by O. Wallach[1] who had prepared the optically inactive modification by the reduction of nitrosopinene.

The properties of the l-pinocamphone obtained from hyssop oil are as follows: b. p. 212 to 213° (752 mm.); $d_{15°}$ 0.9662; α_D — 13°42′; $n_{D20°}$ 1.47421; mol. refr. 44.40.

The semicarbazone melts at 228 to 229° and is difficultly soluble in alcohol. In addition there was isolated in small amount, a more readily soluble semicarbazone that melted at 182 to 183°. However, the same ketone appears to underlie both semicarbazones, for upon hydrolysis with sulphuric acid the same odor was produced. The oxime boils at 105 to 110° (4 mm.) and is a colorless oil from which, in the course of time, crystals separate, which, when purified on a porous plate, melt at about 37 to 38°.

Especially characteristic is the well-crystallizing dibromide $C_{10}H_{14}OBr_2$ which results in excellent yield and which melts without decomposition at 93 to 94°. It ought to prove especially suitable for purposes of identification. Reduced by means of zinc dust in glacial acetic acid, the ketone is readily regenerated.

The alcohol obtained by reduction of the alcoholic solution of the ketone with sodium, has a camphor-like odor. It boils at 217 to 218° and crystallizes in long needles that melt at at 67 to 68°.

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[1] Liebig's Annalen 300 (1898), 287; 346 (1906), 235; 360 (1908), 92.

Oxidized with permanganate, the ketone yields l-*pinonic acid* with a good yield. Recrystallized from petroleum ether this acid melts at 69.5 to 70.5°. The semicarbazone crystallizes in well-developed octahedra, with strong refractive capacity, that melt at 204°. The semicarbazone crystallizes in needles that melt at 129 to 129.5°. With sulphuric acid this ketoacid undergoes quantitatively intramolecular rearrangement to the lævogyrate modification of methoethyl heptanonolid. This compound crystallizes in quadrangular plates that melt at 46 to 47°. In addition to the ketoacid, the oxidation of the ketone yielded an acid which crystallized in shiny small crystals that melted at 189 to 190°. In all probability they are the active form of the isomeric camphoric acid, $C_{10}H_{16}O_4$ which Wallach obtained from *i*-pinocamphone.

With the aid of the acid phthalate very small amounts of an alcohol boiling at 221 to 222° and having a pleasant odor could be extracted from hyssop oil. The higher boiling portions seemed to consist of sesquiterpene derivatives.

Cineol was not present in the oil. Inasmuch as hyssop oil is not infrequently adulterated with spike oil it would seem possible that the occurrence of cineol observed by Genvresse and Verrier was due to this circumstance.

804. Oil of Sweet Marjoram.

Oleum Majoranæ. — Majoranöl. — Essence de Marjolaine[1]).

Origin. The fresh, flowering herb of *Majorana hortensis,* Mch. (*Origanum Majorana,* L.) yields upon distillation 0.3 to 0.4 p.c., the dry herb 0.7 to 3.5 p.c. of volatile oil. The commercial oil comes for the most part from Spain.

Properties. Oil of sweet marjoram is a yellowish or greenish-yellow liquid of a pleasant odor reminding at the same time of cardamom and sweet marjoram. The taste is spicy and mild. $d_{15°}$ 0.894 to 0.910; α_D + 15 to + 19°; $n_{D20°}$ 1.473 to 1.476; A. V. up to 0.8; E. V. 10 to 30; soluble in 1 to 2 vol. and more of 80 p.c. alcohol.

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[1]) Concerning the French designation "marjolaine", which is applied to *Majorana hortensis* as also to *Origanum vulgare* and *Calamintha Nepeta* comp. E. M. Holmes, Perfum. Record 3 (1912), 322.

A number of Cyprian oils which had a relatively faint odor and mostly were light in color, have been examined in the laboratory of Schimmel & Co. Their properties are similar to those of the Spanish oils described above. $d_{15°}$ 0.897 to 0.906; α_D + 12 to + 14°; $n_{D20°}$ 1.4750 to 1.4755; A. V. up to 0.6; E. V. 5 to 12; soluble in about 1 vol. and more of 80 p.c. alcohol.

The Imperial Institute[1]) in London reports on three similar oils; two had been obtained from Cyprus, the third had been distilled in London from dry herb (yield 3.05 p.c.) The latter had practically the same constants ($d_{15°}$ 0.888; α_D + 13° 15'; S. V. 12.8; soluble in 8 to 9 vol. of 80 p.c. alcohol) as those of the Cyprus oils ($d_{15°}$ 0.899 and 0.9126; α_D + 14° 2' and + 3° 45'; S. V. 6.4 and 8.25; soluble in 1.3 and 1 vol. respectively of 80 p.c. alcohol). The London oil contained 2 p.c. of phenols, the two Cyprus oils were free from phenol.

The herb was identified by O. Stapf as *Origanum majoranoides*, Willd.[2]) and by E. M. Holmes as *O. Maru*, L.

An oil distilled from dry herb from Beyroot (yield 3.69 p.c.) had the following constants: $d_{15°}$ 0.9088; α_D + 16° 26'; $n_{D20°}$ 1.4758; A.V. 0.6; E.V. 12.9; E.V. after acetylation 75.3; soluble in 3 vol. and more of 80 p.c. alcohol.

Composition. Oil of sweet marjoram has repeatedly been subjected to chemical investigation.

The stearoptene described and analyzed by G. J. Mulder[3]) presumably was nothing more or less than terpin hydrate which was formed under favorable conditions in a water-containing oil.

According to G. Bruylants[4]) the oil is said to consist of 5 p.c. of a dextrogyrate hydrocarbon, $C_{10}H_{16}$, and 85 p.c. of a dextrogyrate mixture of borneol and camphor. The latter statement could not be verified.

[1]) Bull. Imp. Inst. 11 (1913), 50.

[2]) According to Holmes (Perfum. Record 4 [1913], 41) *Origanum majoranoides*, Willd. is botanically closely related to *Origanum Majorana*, L. A difference, however, exists in this that the former is perennial and the latter annual. According to the Index Kewensis both names are synonymous.

[3]) Liebig's Annalen 31 (1839), 69, — Journ. f. prakt. Chem. 17 (1839), 103.

[4]) Journ. de Pharm. et Chim. IV. 30 (1879), 138; Jahresb. f. Pharm. 1879, 160; Chem. Zentralbl. 1879, 616.

F. Beilstein and E. Wiegand[1]) isolated a terpene boiling at 178° which had a specific gravity of 0.846 at 18.5°. It absorbed a molecule of hydrogen chloride without, however, yielding a solid compound. That portion of the oil which boiled between 200 and 220° they regarded as a sesquiterpene hydrate $C_{15}H_{24} \cdot H_2O$, because of the analytical results obtained. The low boiling point, however, renders this assumption improbable.

According to the investigation of W. Biltz[2]), sweet marjoram oil contains about 40 p.c. terpenes, principally *terpinene,* the presence of which was established by the preparation of its nitrosite melting at 155 to 156°. As further constituent d-*α-terpineol* was found but it could not be crystallized. Fraction 215 to 218° (d 0.920), the elementary analysis of which agreed with the formula $C_{10}H_{18}O$, upon oxidation with potassium permanganate, yielded trihydroxy hexahydrocymene, $C_{10}H_{20}O_3$, which melted at 129 to 130°[3]). Further oxidation with chromic acid and sulphuric acid yielded a small amount of the ketolactone $C_{10}H_{16}O_3$, m. p. 61°, which O. Wallach had obtained upon oxidation of terpineol. According to the results, fraction 215 to 218° of sweet marjoram oil must contain *α*-terpineol.

According to Wallach[4]), the bulk of the marjoram terpineol consists of an isomer, namely of the active *terpinenol-4* (Δ^1-men-thenol-4). (Comp. vol. I, p. 382.)

Oxidized with potassium permanganate, it yielded a glycerol $C_{10}H_{17}(OH)_3$ (1,2,4-trihydroxyterpane) which, when recrystallized from chloroform, yields needle-shaped crystals that melt at 114 to 116°. Heated carefully, water is split off, and a substance sublimes that melts at 129°. Distilled with aqueous hydrogen chloride it yields cymene and carvenone.

The alcohols of the marjoram oil are contained in it, for the most part as such, and only in small part as ester.

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[1]) Berl. Berichte 15 (1882), 2854.

[2]) *Über das ätherische Öl von Origanum Majorana.* Inaug.-Dissert., Greifswald 1898; Berl. Berichte 32 (1899), 995.

[3]) The substance obtained by Wallach from inactive terpineol melts at 121 to 122° (Liebig's Annalen 275 [1893], 152).

[4]) Liebig's Annalen 350 (1906), 169; 356 (1907), 206.

805. Oil of Origanum vulgare.

The oil distilled from the herb of *Origanum vulgare,* L.,
Ger. *Dostenöl,* finds very little practical application. Computed
with reference to the dry herb, the yield is 0.15 to 0.4 p.c. The
oil possesses a strongly aromatic odor and a spicy, bitter taste[1]).
$d_{15°}$ 0.870 to 0.910; α_D — 34.4°[2]).

According to R. Kane[3]) the oil contains a stearoptene con-
cerning which, however, further information is wanting. The bulk
of the oil is said to boil at 161°. In an oil distilled from the
fresh herb, E. Jahns[2]) found two phenols, one of which gave a
green color test with ferric chloride and which presumably is
identical with carvacrol, the other a violet color reaction with
the same reagent. Both phenols, however, do not constitute
more than 0.1 p.c. of the oil.

French origanum oils of commerce are mostly compositions
with a pulegium-like odor which possibly do not contain a trace
of genuine oil.

806. Oil of Cretian Origanum.

Oleum Origani Cretici. — Spanish Hopfenöl. — Essence d'Houblon d'Espagne.

By the above names (also Ger. *Kretisch Dostenöl*) several
carvacrol-containing oils are designated that are obtained from
Origanum species indigenous to the Mediterranean countries.

On account of the numerous species of this genus, it is
difficult for the most part to determine accurately the botanical
origin of individual oils. This is especially true because the
experts themselves do not always agree as to the characteristics
of the several species. This becomes apparent from the exami-
nation by two well-known botanists of an Origanum species[4])
distilled in the island of Cyprus and in the Imperial Institute in
London. O. Stapf pronounced it to be *Origanum majoranoides,*
Willd., and E. M. Holmes as *O. Maru,* L.

Frequently it may also occur that the commercial oils are
not distilled exclusively from a single species. Hence con-

[1]) Report of Schimmel & Co. April 1891, 62.
[2]) Arch. der Pharm. 216 (1880), 277.
[3]) Liebig's Annalen 32 (1839), 284. — Journ. f. prakt. Chem. 15 (1838), 157.
[4]) Bull. Imp. Inst. 11 (1913), 50.

tradictory results of the physical and chemical examination of apparently the same oils may be due to one or both of the above-mentioned causes.

Formerly it was assumed that carvacrol was the characteristic constituent of Cretian origanum oil (See first edition of the book p. 622). At present oils of this class are known the phenol of which consists entirely or in part of thymol, as is the case with the oil of thyme. It remains to be ascertained whether one and the same plant is capable of producing one and then the other phenol under different conditions.

1. ORIGANUM OIL FROM TRIESTE.

Origin. This variety formerly entered commerce via Trieste. It is uncertain whether it was distilled there or in the islands of the Mediterranean which supply the herb. The oil corresponded in all its properties with that distilled in Germany from the dry herb of *Origanum hirtum,* Lk. which was examined by E. Jahns[1]). Hence it is assumed that the commercial oils were derived from the same plant. From the dry herb a yield of 2 to 3 p.c. was obtained.

Properties. The oil has a pungent, thyme-like odor and a biting, persistent taste. Freshly distilled it is of a golden-yellow color, which, however, becomes dark brown to blackish when the oil is exposed to the air. The coloration begins at the surface and gradually passes downward. $d_{15°}$ 0.94 to 0.98. On account of the dark color, the optical rotation cannot for the most part be determined. In the few instances in which the action upon polarized light could be observed, it was found to be inactive, or slightly lævogyrate or even slightly dextrogyrate. The oil dissolves in 2 to 3 vol. of 70 p.c. alcohol to a clear solution. It contains 60 to 85 p.c. carvacrol.

Composition. An oil of this class that had been distilled from dry herb in Germany and the botanical source of which had been determined by Grisebach as *Origanum hirtum,* Lk., was examined by E. Jahns[1]). He showed that its principal constituent is *carvacrol,* a phenol which had previously been prepared artificially from carvone, but which at that time had not been found in an oil.

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[1]) Arch. der Pharm. **215** (1879), 1.

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As he shook out with ether the phenol sodium solution which he had obtained by treating the oil with dilute sodium hydroxide solution, he extracted all of the carvacrol. Upon acidulating this alkaline solution, which no longer yielded any-thing to ether, he obtained a very small amount, scarcely more than 0.2 p.c., of a second phenol which gave a violet color with ferric chloride, but which was not farther investigated.

The non-phenol constituents of the oil, after repeated recti-fication over sodium, boiled for the most part between 172 and 176°. As shown by the formation of cymene-sulphonic acid, they consisted principally of *cymene*. From the fact that the fraction, when shaken with concentrated sulphuric acid, became strongly heated with development of sulphur dioxide, it became apparent that the fraction contained other substances, presumably terpenes, besides cymene.

S. Pickles[1]) has examined an oil of entirely different com-position, though according to determination made by the botanical Institute at Kew, it was likewise derived from *O. hirtum*, Lk. The material to be distilled was collected by the Commercial Museum at Trieste and yielded 3.3 p.c. of oil, $d_{15°}$ 0.9440; $\alpha_D + 0°24'$; soluble in 2.8 vol. of 70 p.c. alcohol; phenol con-tent 64.4 p.c. Contrary to the observations made in connection with the above oil, the phenol consisted principally of *thymol*. Carvacrol was not present.

Three oils distilled[2]) in the Dalmatian islands Curzola and Lissa, likewise contained thymol only. According to Dr. Giessler, custodian of the Botanical Institute of the University at Leipzig, the herb was that of *Origanum hirtum*, Lk. *a albiflorum*. $d_{15°}$ 0.9231 to 0.9400; $\alpha_D + 0°6'$ to $0°20'$; $n_{D20°}$ 1.49394 to 1.50436; soluble in 1.3 to 2.8 vol. and more of 80 p.c. alcohol. Thymol content 57 to 60 p.c.

2. ORIGANUM OIL FROM SMYRNA.

Origin. This oil is distilled in Asia Minor[3]) and presumably elsewhere, from the herb of *Origanum smyrnæum*, L. (*O. Onites*, L.,

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[1]) Bull. Imp. Inst. 9 (1911), 388. — Proc. Chem. Soc. 27 (1911), 284.

[2]) Report of Schimmel & Co. October 1911, 63.

[3]) This is possibly the same oil which is distilled in primitive apparatus in Konia, Anatolia, and sold in the streets of Constantinople in small flasks as a remedy against rheumatism. Comp. Report of Schimmel & Co. April 1891, 56.

Majorana Onites, [L.] Benth.) and enters commerce at Smyrna. The yield from the dry herb is 1.4[1]) to 2.4 p.c.[2]).

Properties. The oil is of a golden-yellow to brown color and has a mild odor reminding somewhat of linaloe oil or linalool. $d_{15°}$ 0.898 to 0.960; α_D — 1 to — 14°; $n_{D20°}$ 1.495 to 1.523; soluble in 2 to 3 vol. and more of 70 p.c. alcohol. The phenol content fluctuates greatly, *viz.,* from 16 to 74 p.c. and for the most part lies between 25 and 45 p.c. In reverse proportion thereto is the linalool content that fluctuates between 20 to 50 p.c. (determined by fractionation). The specifically light oils are mostly the ones richest in linalool.

Composition. The Smyrna oil mostly differs from the Trieste oil by its linalool content which is not unappreciable. As a result the phenol content is lower. According to an investigation by E. Gildemeister[3]) there is present, in addition to very much *carvacrol* (m.p. of phenyl urethane 140°), very little phenol colored violet by ferric chloride which has already been mentioned in connection with the Trieste oil. Fraction 155 to 163° (α_D — 3°28′) has the remarkably low specific gravity of 0.826 at 15°. For this reason the presence of a so-called olefinic terpene is suspected.

Upon oxidation of fraction 175° hydroxy *iso*propyl benzoic acid, m.p. 156 to 158°, was obtained. Boiled with fuming hydrochloric acid this was converted into *iso*propenyl benzoic acid, m.p. 257 to 262°, thus proving the presence of *cymene.* Fraction 198 to 199° ($d_{15°}$ 0.870; α_D — 15°56′) possessed all of the properties of l-*linalool.* Its presence was proven by oxidation with chromic acid mixture resulting in the formation of citral. The identity of this aldehyde was proven in the usual manner by converting it into citryl-β-naphthocinchoninic acid, m.p. 198 to 199°.

As reported by Schimmel & Co.[4]) *cedrol* (cedar camphor) crystallized from the highest boiling fractions. This amounted to about 5 p.c. of the original oil. Purified by suction and pressure from adhering oil and recrystallized from dilute alcohol, it was obtained in needle-shaped crystals melting at 81 to 84°.

[1]) Bull. Imp. Inst. 9 (1911), 388.

[2]) Observation made by Schimmel & Co.

[3]) *Über Smyrnaer Origanumöl.* Arch. der Pharm. 33 (1895), 182.

[4]) Report of Schimmel & Co. October 1906, 48.

After further recrystallization from petroleum ether it melted fairly constantly at 85.5 to 87°; $[\alpha]_D + 8°48'$ (in 10 p.c. chloroform solution). A depression of the melting point of a mixture of the sesquiterpene alcohol described above with cedar camphor did not take place. Its phenyl urethane melted at 106 to 107°.

Whether the cedar camphor was a natural constituent of the oil or was present because of adulteration with oil of cedar could not be determined. In two oils[1]), which were examined later, cedar camphor could not be detected. In connection with one of these oils the presence of previously isolated constituents was verified, partly by means of new derivatives. The presence of *α-pinene* in the lowest, slightly lævogyrate fraction ($\alpha_D -1°56'$) was demonstrated by its nitrolbenzylamine melting at 123.5 ; likewise that of d-*camphor* by means of its lævogyrate oxime melting at 120°. Of carvacrol its nitroso compound melting at 153°, of *l*-linalool its phenyl urethane (m.p. 63 to 64°) were prepared.

3. CYPRIAN ORIGANUM OIL.

Origin. The botanical origin of the origanum oil distilled in fairly large quantities in Cyprus is still in doubt. On the island the plant yielding the oil is known as *Ρίγανη*[2]). Gennadius[2]), the former Director of the Board of Agriculture in Cyprus, regards it as *Origanum Onites.* Holmboe[2]), who visited the island as representative of the University of Christiania, regards it as *O. dubium,* a subspecies of *O. Maru,* L., whereas Holmes[3]) regards it as *O. majoranoides,* Willd., a variety of *O. Maru,* L. According to D. Saracomenos[4]) the plant grows wild in the northwestern part of the island.

The distillation begins in July or somewhat sooner, when the seeds are mature, and lasts until the middle of December. In order to obtain one *oke* of oil (= $2^2/_3$ lbs. or a quart), 30 to 45 *okes* of origanum herb are required. The oil distilled from fresh plants has a dirty gray color, whereas the oil distilled from plants that have been stacked for a month, is of a dirty

[1]) Report of Schimmel & Co. April 1911, 84.

[2]) S. Pickles, Journ. Chem. Soc. 93 (1908), 862.

[3]) Pharmaceutical Journ. 79 (1907), 378. — Perfum. Record 4 (1913), 41.

[4]) Chemist and Druggist 70 (1907), 365.

red, a color that is likewise assumed .in the course of time by the oil distilled from fresh plants.

In 1909 there were produced 1772 lbs.[1]) and in 1910 as much as 2842 lbs.[2]) of Cyprian origanum oil. It is also designated oil of thyme but erroneously[3]).

Properties. The oil which is originally of a light color rapidly becomes dark under the influence of air. $d_{15°}$ 0.962 to 0.967; $\alpha_{\rm l}$, inactive or slightly dextrogyrate, up to $+0°20'$; soluble in 2 to 3 vol. and more of 70 p.c. alcohol; phenol content (carvacrol) 70 to 84 p.c.[4])[5]).

Composition. According to Francis[6]), the Government analyst, Cyprian origanum oil consists principally of a mixture of thymol, thymene and cymene whereas the phenols of the oils examined by the Imperial Institute of London and by Schimmel & Co. were identified as *carvacrol*.

Saracomenos[6]) determined the thymol content of the oils examined by Francis gravimetrically. In the dark oil he found 79 p.c. and in the light oil 83 p.c.

Pickles[6]) suspects that these analyses merely represent the result of fractionation without farther chemical characterization of the constituents. Moreover, Francis appears to have regarded the oil in question as a thyme oil and consequently assumed that the carvacrol was thymol. The fraction pronounced hy him as thymene possibly should be regarded as *l*-pinene.

In a Cyprian oil Pickles[6]) found traces of an acid with the odor of iso*butyric acid,* also 84 p.c. of *carvacrol* (m.p. of nitroso compound 153 to 154°; m.p. of phenylurethane 140°). In addition he found small amounts, about 0.2 p.c., of a *phenol* $C_{11}H_{16}O_2$ which yielded a handsome purple color reaction with ferric chloride and which probably was a hydroxy methoxy cymene.

From the non-phenol portion of the oil there was separated a fraction 160 to 164° (750 mm.) with a lemon-like odor (2.5 p.c.

[1]) Chemist and Druggist 75 (1909), 834.
[2]) Bull. Imp. Inst. 10 (1912), 148.
[3]) J. C. Umney, Chemist and Druggist 75 (1909), 452.
[4]) S. Pickles, Journ. Chem. Soc. 93 (1908), 862.
[5]) Bull. Imp. Inst. 4 (1906), 297. — Report of Schimmel & Co. April 1907, 100.
[6]) *Loc. cit.*

.of the oil) $d_{16°}$ 0.847; n_D 1.480; and $\alpha_D +1° 50'$. It was regarded as an unknown terpene and named *origanene*. The hydrocarbon yielded a nitrosochloride melting at 91 to 94° from which a nitrolbenzylamine (m.p. 104 to 105°) and a nitrolpiperidide (m.p. 198°) were prepared. After shaking with dilute sulphuric acid for several days terpin hydrate, m.p. 118 to 119°, resulted, which yielded dipentene dihydroiodide with hydrogen iodide. From the mother liquid of the terpin hydrate crystal mixtures were obtained, a fraction melting between 126 and 131°. Pickles suggests a formula for origanene which, however, corresponds with Wallach's formula for α-terpinene.

Fraction ·174 to 175° consisted of *cymene* (m.p. of p-hydr-. oxy*iso*propyl benzoic acid 156 to 157°; m.p. of *iso*propenyl benzoic acid 256 to 257°). In addition to origanene and cymene a third hydrocarbon was present which added two molecules of hydrogen chloride. However, no crystalline derivative was obtainable, hence it could not be further characterized. These hydrocarbons constituted about 8.5 p.c. of the oil.

Fraction 110 to 120° (10 to 15 mm.) constituted about 3.5 p.c. of the oil, had an agreeable odor of menthol and camphor, the composition $C_{10}H_{18}O$ and the following constants: $d_{14°}$ 0.934; $\alpha_D -4°$. The examination for ketones and esters yielded negative results. It appeared to be a terpene alcohol similar to terpineol, from which phenyl*iso*cyanate and phthalic acid anhydride readily split off water and which yielded terpin hydrate when shaken with dilute sulphuric acid. The higher-boiling fractions, about 1.3 p.c. of oil, seemed to consist of a mixture of oxygenated constituents. Methoxy- and ethoxy compounds were not present, of esters small amounts at most.

4. SYRIAN ORIGANUM OIL.

· **Origin.** This oil is probably obtained from *Origanum Maru*, L., which is indigenous to the countries of the eastern Mediterranean, such as Syria, Palestine, and Tripolis. · The material which Schimmel & Co. had obtained from their agent, which according to him is the source of the oil, had been sent to E. M. Holmes[1]), who recognized it as the herb of *O. Maru*, L.

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[1]) Perfum. Record 4 (1913), 71.

The varying composition of the oil, sometimes containing thymol, sometimes carvacrol, leads one to suspect that different species are used in Syria for distillation.

Properties. $d_{15°}$ 0.930 to 0.960 (in one instance 0.977); α_D —0° 50′ to +1° 35′, mostly dextrogyrate; phenol content 57 to 74 p.c.; in most cases soluble in 2 to 3 vol. of 70 p.c. alcohol, the addition of more solvent almost always causing opalescence and even turbidity.

Composition. In connection with the oils that first appeared in the market Schimmel & Co. [1] found that the phenols consisted exclusively of *carvacrol* [2]), oils examined later contained either *thymol* [3]) alone or thymol and carvacrol.

From an oil examined by Roure-Bertrand Fils [4]) there separated upon standing a transparent substance, possibly cedar camphor.

5. SICILIAN ORIGANUM OIL.

For a Sicilian oil, possibly from *Origanum creticum* [5]), Umney and Bennett [6]) report the following constants: $d_{15°}$ 0.920; α_D ±0°; phenol content 44 p. c., principally carvacrol; soluble in 2 vol. of 80 p.c. alcohol; does not yield a clear solution with 70 p.c. alcohol. 48 p.c. of the oil distilled below 220°.

6. GREEK ORIGANUM OIL.

In connection with a Greek oil, Evans Sons Lescher and Webb Ltd. [7]) determined the following constants: $d_{15.5}$ 0.9351; α_D ±0°; $n_{D20°}$ 1.502; phenol content 63 p.c.; soluble in 4 vol. and more of 70 p.c. alcohol.

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[1]) Report of Schimmel & Co. April 1907, 73. — Berichte von Roure-Bertrand Fils April 1911, 24.

[2]) Report of Schimmel & Co. April 1907, 73.

[3]) *Ibidem* October 1911, 63.

[4]) *Loc. cit.*

[5]) Umney and Bennett fail to give the author's name. The *Index Kewensis* records: *Origanum creticum*, L. = *O. vulgare*, L., *O. creticum*, Schousb. ex Ball. = *O. compactum*, Benth., and *O. creticum*, Sieber ex Benth. = *O. hirtum*, Link.

[6]) Pharmaceutical Journ. 75 (1905), 860. — Chemist and Druggist 67 (1905), 970.

[7]) Analytical Notes 1910; Report of Schimmel & Co. April 1911, 84.

807. Oil of Origanum floribundum.

Battandier[1]) found that the volatile oil of *Origanum flori-bundum*, Munby (*O. cinereum*, De Nöe) yields, upon shaking, about one-fourth of its volume to alkali. The separated phenol crystallizes almost completely when touched with a thymol crystal, hence consists principally of *thymol*. The small residue of liquid phenol appears to be carvacrol.

808. Oil of Pycnanthemum lanceolatum.

The oil of the herb of *Koellia lanceolata* (Pursh), O. K. (*Pycnanthemum lanceolatum*, Pursh; *Thymus virginicus*, L.)[2]), known as mountain mint, can scarcely be distinguished as to odor from American pennyroyal oil. $d_{15°} 0.918$[3]) to 0.936[4]); $d_{20°} 0.914$ to 0.935; $\alpha_D - 0.566$ to $+ 11.083°$[5]).

According to Correll[4]) it contains 7 to 9 p.c. of *carvacrol* (m.p. of carvacrol sulphonic acid 56 to 57°; m.p. of dicarvacrol 145 to 147°). The non-phenol oil distilled between 180 to 230°. The analysis of fraction 220 to 230° ($d_{20°} 0.922$; $[\alpha]_D + 14.88$°), which had a mint-like odor, corresponded with the formula $C_{10}H_{16}O$ and suggested *pulegone*. The identity of this ketone was established by Alden[5]) who prepared the pulegone oxime hydrate. He obtained crystals melting at 151°, which after cooling and congealing, melted at 117 to 118° when heated a second time. The melting point of pulegone oxime hydrate, the pulegone oxime of Beckmann and Pleissner, is at 156 to 157°, that of Wallach's normal oxime at 118°.

809. Oil of Pycnanthemum incanum.

This oil was distilled with a yield of 0.98 p.c. from the dry herb of *Koellia incana* (Mchx.), Baill. (*Pycnanthemum incanum*, Mchx.) known in North America as mountain mint or basil[6]). It had a reddish-yellow color and a strongly aromatic odor; d 0.935; yields a clear solution with 2 vol. of 70 p.c. alcohol.

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[1]) Journ. de Pharm. et Chim. VI. 16 (1902), 536.

[2]) *Pycnanthemum lanceolatum* and *P. linifolium* were formerly regarded as one and the same species and described as *Thymus virginicus*, L.

[3]) H. C. Barker, Americ. Journ. Pharm. 66 (1894), 65.

[4]) W. G. Correll, Pharm. Review 14 (1896), 32.

[5]) F. W. Alden, *ibidem* 16 (1898), 414.

[6]) Report of Schimmel & Co. October 1893, 45.

810. Oil of Thyme.

Oleum Thymi. — Thymianöl. — Essence de Thym.

Origin. French oil of thyme is distilled principally from the fresh, flowering herb in the mountains of southern France, where *Thymus vulgaris*, L. grows abundantly. It is the same territory in which rosemary oil[1]) is produced. The distillation is carried on in May and June. The small woody stems of thyme are found in open woods as well as in shadeless coast districts of the Riviera, also in the mountainous regions of the Maritime Alps to an altitude of 1000 m.

From which plant Spanish oil of thyme is distilled is uncertain. Its character and composition which rather resemble those of origanum oil *(Spanisch Hopfenöl /Kretisch Dostenöl/)* suggest a different botanical source. However, inasmuch as there are Spanish thyme oils which resemble the French as to properties, it may be assumed that in different districts different species of thyme are distilled.

Algerian oil of thyme which is produced principally in the province of Oran[2]) is distilled from the herb of *Thymus algeriensis*, Boiss. et Reut. *(Th. ciliatus,* Benth.)[3]).

So-called Cyprian oil of thyme is an origanum oil and has been described as such on p. 486 *(Spanisch Hopfenöl)*.

The yields obtained from oil of thyme have reference to the distillations of cultivated herb, from which, however, the commercial oil is not obtained as a rule. Fresh German herb yields 0.2 to 0.5 p.c., dry 0.4 to 1.7 p.c. of oil; fresh French plants cultivated in Germany yielded 0.9 p.c., dry herb 2.5 to 2.6 p.c of oil. For Algerian oil a yield of 1.5 p.c. (from dry herb?) is recorded[3]).

Properties. French oil of thyme (like the German, which however, is of little or no commercial importance) is a dirty dark reddish-brown liquid, of a pleasant, strong odor of thyme and a pungent, sharp, persistent taste. The specific gravity of a pure oil is invariably above 0.900, that of good French oils

[1]) Berichte von Roure-Bertrand Fils October 1900, 25.

[2]) *Ibidem* October 1906, 42.

[3]) Bull. mensuel de l'office du gouv. Tunisien; according to Journ. Parfum et Savonn. 22 (1909), 6; Report of Schimmel & Co. April 1909, 107.

mostly between 0.905 and 0.915. In connection with their own distillates of fresh and dry herb Schimmel & Co. observed 0.909 to 0.935. The optical rotation is slightly lævogyrate, up to $-4°$, but for the most part cannot be determined because of the dark color of the oil. It dissolves in $^1/_2$ vol. of 90 p.c. alcohol and in 1 to 2 vol. of 80 p.c. alcohol, of 70 p.c. alcohol from 15 to 30 vol. are mostly required to effect a clear solution. In normal oils the phenol content is mostly 20 to 30 p.c., rarely up to 42 p.c. As a rule the phenol of French and German oils is thymol, some-times, however, carvacrol or a mixture of both.

Oil of thyme rectified in the ordinary manner quickly resumes the dark color of the crude oil. In order to obtain a light yellow oil with full phenol content special precautions have to be exer-cised during rectification.

· Inasmuch as the consumers are apt to lay unnecessary stress on the color of the oil, in southern France oil of thyme is frequently distilled with several volumes of turpentine oil. Hence so-called white oil of thyme of commerce is mostly nothing more or less than a turpentine oil containing a small portion of oil of thyme. Frequently their thymol content is 1 to 2 p.c., rarely as high as 5 p.c. This explains the remarkable fact that rectified oil of thyme is frequently quoted a lower price than the crude oil.

Very different from the French and German oils of thyme is the Spanish, the color of which is frequently a dark green. The specific gravity lies between 0.930 and 0.956; $\alpha_D + 1°30'$ to $-3°$, mostly lævogyrate; n_{D20} 1.504 to 1.510. The phenol content is 50 to 74 p.c. and consists exclusively of carvacrol and no thymol. It is further distinguished from the French and German oils by its greater solubility, for it yields a clear solution with 2 to 3 vol. of 70 p.c. alcohol. These striking differences render a different botanical origin of the Spanish oil probable.

More recently, however, Spanish oils have entered commerce from Malaga, Granada, Barcelona, etc. the composition of which approximates that of the French oils, more particularly in so far as they contain thymol and no carvacrol. d_{15} 0.909 to 0.940; $\alpha_D - 0°25'$ to $-8°20'$; n_{D20} 1.491 to 1.499; soluble in 2 to 4 vol. and more of 80 p.c. alcohol. Thymol content 20 to 53 p.c.

Composition. As the value of cassia oil is given by its cinnamic aldehyde content, that of clove oil by its eugenol content, that

Fig. 38.   Distillation of thyme oil in Spain.

of bergamot oil by its linalyl acetate content, so the value of oil
of thyme is given by its thymol (or carvacrol) content. Although
thymol was observed as early as 1719, hence is one of the oldest
of known volatile oil constituents, its composition was not correctly
determined until 1853 by A. Lallemand[1]). He established the
commonly accepted formula $C_{10}H_{14}O$ as against $C_{10}H_{15}O$ previously
proposed by L. Doveri[2]).

Occasionally thymol crystallizes from old oils in the cold.
Completely it can be separated only by shaking it out with caustic
lye. It melts at 50° to 51.5° and boils at 232°. Its properties and
characteristic derivatives have been described in vol. I p. 471.

However, thymol is not the only phenol in oil of thyme. At
times it is replaced in part, at times it appeares to be replaced
entirely by its isomer carvacrol (for its properties see vol. I,
p. 473). What conditions favor the occurrence of the one and
what that of the other has not been ascertained. Schimmel & Co.
record the following observations in connection with oils distilled
by themselves: French, dry herb yielded an oil that contained much
thymol and little carvacrol. The distillation of fresh French herb
raised in Germany yielded an oil, the phenol of which consisted
exclusively of carvacrol. Both fresh and dry German thyme
yielded oil containing thymol only. Most of the Spanish oils contain
carvacrol only and no thymol. This phenol content (see Properties)
is also much larger than that of any other oil of thyme.

That oil of thyme probably contains a third phenol becomes
apparent from the greenish-black color produced in the oil upon
the addition of ferric chloride.

Other constituents found in oil of thyme by Lallemand are:
cymene, $C_{10}H_{14}$, b. p. 175°, and *thymene,* $C_{10}H_{16}$, boiling between
160 and 165° and lævogyrate. Inasmuch as Schimmel & Co.[3])
have established the identity of this hydrocarbon with l-*α-pinene,*
the term thymene should be dropped. *l*-Pinene is present in thyme
oil in small amounts only, so that its presence can be established
only then when larger amounts of oil are available.

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[1]) Compt. rend. 37 (1853), 498. — Liebig's Annalen 101 (1857), 119. —
Annal. de Chim. et Phys. III. 49 (1857), 148. — Liebig's Annalen 102 (1857), 119.

[2]) Annal. de Chim. et Phys. III. 20 (1847), 174. — Liebig's Annalen 64
(1848), 374.

[3]) Report of Schimmel & Co. October 1894, 56.

Fig. 39. Distillation of thyme oil in Spain.

H. Labbé[1]) did not succeed in obtaining a solid hydrochloride from fraction 155 to 158°. With amyl nitrite and hydrochloric acid he obtained a nitrosochloride melting at 106.5° (the melting point of pinene nitrosochloride is 103°, but frequently it is higher), hence he concludes that pinene is not a constituent of oil of thyme. The preparation of either the benzylamine or piperidine derivatives could have removed his doubts. In fraction 165 to 169° Labbé claims to have found *menthene*. He obtained a nitrosochloride melting at 113 to 113.5°, and upon oxidation of the fraction with permanganate cymene resulted. As a matter of fact the melting points of the nitrosochlorides are totally unsuited for the characterization of hydrocarbons, unless their preparation is supplemented by that of nitrolamines. This, however, was neglected. The fact that cymene was obtained proves nothing since this hydrocarbon is a constituent of the oil and may have preexisted in the fraction examined.

Of the more difficultly volatile, non-phenol constituents of the oil, fraction 195 to 230°[2]) possessed a distinct odor of borneol and linalool. Inasmuch as a separation of these two substances by distillation could not be effected because of the proximity of their boiling points, this fraction was oxidized with chromic acid and the oxidation product distilled in vacuum. One part of the distillate congealed and was shown to be *camphor* by its melting point at 176° and its oxime (m. p. 117 to 118°). The liquid portion yielded a crystalline compound upon shaking with sodium bisulphite solution. Washed with alcohol and ether and decomposed with caustic soda, a liquid with a decided odor of citral separated. The citryl-β-naphthocinchoninic acid prepared therefrom melted at 197°. Hence the oxidation products of fraction 195 to 230° of thyme oil are camphor and citral. The formation of the former presupposes the presence of *borneol,* that of the latter *linalool.* The occurrence of linalool was later verified by Labbé[3]) by converting this alcohol into geraniol (m. p. of silver geranylphthalate 133°). Upon oxidation of the borneol fraction Labbé likewise obtained camphor.

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[1]) Bull. Soc. chim. III. 19 (1898), 1009.
[2]) Report of Schimmel & Co. October 1894, 56.
[3]) *Loc. cit.*

According to J. Schindelmeiser[1]), crystals had separated from a French oil of thyme that had been kept for a long time in a lead container with a coating of zinc. From alcohol and water they crystallized in well developed, stout columns that melted at 169°. This substance had the composition $C_{10}H_{22}O_3$, was optically inactive and sublimed as low as 80°. With hydrogen bromide in glacial acetic acid solution there resulted a compound $C_{10}H_{16} \cdot 2HBr$ melting at 68°, and with dilute sulphuric acid a liquid that had a limonene-like odor and which seemed to contain a terpinolene. Schindelmeiser is of the opinion that the substance is possibly identical with the one found by Schimmel & Co.[2]) in juniper berry oil which crystallized at 165 to 166° (see vol. II, p. 163).

Examination. The most common adulterant of oil of thyme is oil of turpentine. For the production of the so-called white oil of thyme this form of adulteration is in general practice. The addition of turpentine oil lowers the specific gravity below 0.900 and diminishes the solubility in alcohol. Another consequence is the lowering of the phenol content, hence the determination of the phenol content is of greatest importance in the examination of oil of thyme. A simple method, which possesses sufficient accuracy for all practical purposes has been described in vol. I, p. 590.

A chemical method for the determination of thymol and carvacrol in volatile oils has been worked out by Kremers and Schreiner. It is described in vol. I, p. 594. On p. 595, line 8 from below it should read *iodine solution,* not thiosulphate solution, an error that becomes apparent from the context.

811. Oil of Thymus Mastichina.

Thymus Mastichina, L., which occurs in the Mediterranean region[3]) is known in Spain as forest marjoram *(Mejorana silvestre,* Ger. *Waldmajoran).* Although the plant is cultivated extensively in Spain, and although considerable amounts of the oil are exported, nothing is known about its composition. Authentic samples of the oil have been examined by B. Dorron-

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[1]) Apotheker Ztg. 22 (1907), 853.

[2]) Report of Schimmel & Co. October 1895, 49.

[3]) See M. Willkomm, Grundzüge der Pflanzenverbreitung auf der iberischen Halbinsel, Leipzig 1896.

soro[1]). It is light yellow in color, becomes darker in the course of time and possesses a camphor-like odor reminding of thyme. Its constants are: $d_{20°}$ 0.907 to 0.945; α_D -0°50' to +4°40'; $n_{D28°}$ 1.4630 to 1.4654; S. V. 12.7 to 18.5; ester content 4.44 to 6.47 p.c. (computed as linalyl acetate); E. V. after acetylation 29.2 to 49.3 = 8.2 to 14.09 p.c. alcohol $C_{10}H_{18}O$. It is soluble in all proportions in 94 p.c. alcohol, in 0.5 to 1 vol. of 90 p.c. alcohol and in 1 to 3.7 vol. of 80 p.c. alcohol. In 70 p.c. alcohol it is not always soluble, requiring at times as much as 30 vol.

Of free acids *acetic acid* was identified by its reaction with ferric chloride and its conversion into ethyl acetate, iso*valeric acid* by its boiling point and the preparation of its *iso*amyl ester. The oil contained additional acids, but in such small amounts that they could not be characterized. Acetic and *iso*valeric acids are likewise present as esters. In addition the oil contained a *phenol* (less than 0.1 p.c.) which did not crystallize, gave no color reaction with ferric chloride and no nitroso derivative. From the portions isolated by means of bisulphite (less than 0.1 p.c.) a substance was isolated that had the odor of wine, possibly a ketone. Of terpenes the presence of d-*α-pinene* (7 to 8 p.c.) was proven (b. p. 168° under 710 mm. pressure, m. p. of nitrosochloride 103°; m. p. of nitrolpiperidide 118 to 119°; m. p. of nitrolbenzylamine 122 to 123°). In addition the oil contained very much (64 to 72 p.c.) of *cineol* (addition product with phosphoric acid, m. p. of resorcinol addition product 80°). In fraction 185 to 195° Dorronsoro proved the presence of l-*linalool*, which he characterized by oxidizing it to citral and converting of the latter into β-naphthocinchoninic acid, m. p. 197°.

812. Oil of Wild Thyme.

Oleum Serpylli. — Quendelöl. — Essence de Serpolet.

Origin. *Thymus Serpyllum,* L. (Ger. *Quendel, Feldthymian, Feldkümmel*), which is found in Europe, North America, central and northern Asia, also Abyssinia, yields upon distillation but very little oil. The yield from the dry herb amounts to only 0.15 to 0.6 p.c., less from the fresh.

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[1]) *Contribución al estudio de las esencias españolas. Esencia de mejorana silvestre.* Madrid 1910. Report of Schimmel & Co. April 1911, 111.

Properties. Oil of wild thyme is a colorless or golden-yellow liquid of a pleasant odor reminding of balm and slightly of thyme. $d_{15°}$ 0.890 to 0.920; α_D — 10 to — 21°.

H. Haensel [1]) described a rectified oil of wild thyme: $d_{15°}$ 0.9127; α_D - 11°; S. V. 38; soluble in 1.15 parts of 80 p.c. alcohol. Upon distillation 23.3 p.c. went over up to 200°, 26.7 p.c. above 240°.

In southern France mixtures of the oils of origanum, pennyroyal, spike and thyme are frequently sold as *essence de serpolet,* which naturally have very different properties from those of genuine oil of wild thyme.

Composition. The bulk of the oil distills between 175 to 180° and according to P. Febve [2]) consists of *cymene,* $C_{10}H_{14}$, with which are admixed traces of a dextrogyrate hydrocarbon $C_{10}H_{16}$.

With alkali a small amount of phenol, about 1 p.c., can be shaken out of the oil. The phenol is not a chemical unit, but as shown by E. Jahns [3]), consists of *carvacrol, thymol* and a third phenol which, in alcoholic solution, yields a violet color with ferric chloride but has not been further examined [4]).

The higher boiling fractions, 200 to 250°, contain, in addition to phenols, hydrocarbons, presumably sesquiterpenes.

An oil examined by J. H. Gladstone [5]) had a specific gravity of 0.884 and an optical rotation α_D — 31.6° and consisted almost entirely of a turpentine-like hydrocarbon. This is readily explainable, for according to density and optical rotation the oil had been freely adulterated with French turpentine oil.

813. Oil of Thymus capitatus.

An oil distilled in the province of Granada in southern Spain from the fresh herb of *Thymus capitatus,* Lk., was examined by Schimmel & Co. who report as follows [6]): —

The odor of the oil is strongly thyme-like reminding somewhat of origanum. As to composition it resembles very much.

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[1]) Apotheker Ztg. 19 (1904), 271.
[2]) Compt. rend. 92 (1881), 1290.
[3]) Arch. der Pharm. 216 (1880), 277. — Berl. Berichte 15 (1882), 819.
[4]) E. Buri, Arch. der Pharm. 212 (1878), 485.
[5]) Journ. Chem. Soc. 17 (1864), 1 *et seq.;* Jahresber. d. Chem. 1863, 546 and 549.
[6]) Bericht von Schimmel & Co. October 1889, 56.

the oil from *Satureja Thymbra*. Its specific gravity is 0.901 at 15°; the *thymol* content is small, only about 6 p.c. In addition a liquid phenol is present, the boiling point in vacuum is close to that of thymol (carvacrol?). The other constituents are the same as those of *Satureia Thymbra*. *α-Pinene, cymene, dipentene* and *bornyl acetate* were proven to be present.

814. Oil of Bystropogon origanifolius.

Bystropogon origanifolius, L'Hérit.[1]), a shrub that occurs frequently in the Canary Islands, yields a light yellow oil which resembles that of *Mentha pulegium* as to odor. d_{15} 0.9248; $\alpha_D + 2°57'$; $n_{D20°}$ 1.48229; A. V. 0; E. V. 11.1; E. V. after acetylation 53.83; soluble in 2.5 vol. of 70 p.c. alcohol and in 0.7 vol. of 80 p.c. alcohol. Upon distillation it passes over between 162 and 234°.

The oil contains little l-*limonene* (m. p. of tetrabromide 104°). The bulk of the oil consists of *pulegone* (m. p. of oxime 157°) and some *menthone* (m. p. of semicarbazone 180 to 181°).

815. Oil of Bystropogon mollis.

According to A. Doering[2]), the Argentine mint *Bystropogon mollis*, Kth., yields 0.4 p.c. of volatile oil: d 0.918 to 0.920; it boils principally at 210° and contains about 0.7 p.c. of *free acids*, traces of a *phenol* and 2.5 p.c. of *furfurol*. Menthol does not appear to be present.

816. Cunila Oil.

Cunila origanoides (L.), Briq. (*C. Mariana*, L.[3])), known as dittany in North America, yields 0.7 p.c. of a reddish-yellow oil

[1]) Report of Schimmel & Co. October 1902, 82.

[2]) Bol. Acad. Nac. Ciencias Cordoba 19 (1913), 379; Journ. Chem. Soc. 106 (1914), 1172.

[3]) According to Th. Peckolt (Berichte d. deutsch. pharm. Ges. 14 [1904], 380), the fresh leaves of *Cunila galioides*, Benth. yield 0.174 p.c. of volatile oil with a patchouli-like odor.

that resembles oil of thyme and has a specific gravity of 0.915. A preliminary investigation revealed 40 p.c. of phenol, presumably *thymol*[1]).

817. Lycopus Oil.

The dried herb of *Lycopus virginicus,* Mchx., known in America as wolfstraps and bugle weed, yields 0.075 p.c. of oil on distillation. It has a characteristic but difficultly definable odor. Spec. gr. 0.924 at 15°[2]).

818. Oil of European Pennyroyal.
Oleum Menthæ Pulegii. — Poleiöl. — Essence de Pouliot.

Origin. Commercial European pennyroyal oil is distilled in the Spanish provinces Huelva and Cadiz, in southern France, Algeria, and recently also in Asiatic Turkey from the fresh herb of *Mentha Pulegium,* L. (*Pulegium vulgare,* Mill.). For this purpose the wild plant is mostly used which thrives particularly in moist summers throughout the Mediterranean region. Moreover, it has migrated to South America (Chile). Attempts to cultivate the plant have been made in Sicily[3]), whether successfully or not has not become known.

Properties. Pennyroyal oil has a yellowish to reddish-yellow color, occasionally with a bluish or greenish fluorescence and a strongly aromatic, minty odor. $d_{15°}$ 0.930 to 0.950; α_D +15 to +25°, a low rotation always indicates a low pulegone content; $n_{D20°}$ 1.483 to 1.486; pulegone content (determined according to the sulphite method described in vol. I, p. 589) about 80 p.c. and higher (up to 94 p.c.); soluble in 4 to 7 vol. and more of 60 p.c. alcohol and in 1.5 to 2.5 vol. and more of 70 p.c. alcohol. In a few instances Algerian oils show opalescence in dilute solutions due to paraffin.

Composition. Pennyroyal oil is very uniform in composition. Up to 212° only 5 p.c. pass over, the bulk, about 80 p.c., distills between 212 and 216° and consists principally of a ketone $C_{10}H_{16}O$

[1]) Report of Schimmel & Co. October 1893, 45. — Comp. also Milleman, Americ. Journ. Pharm. 38 (1866), 495.

[2]) Report of Schimmel & Co. October 1890, 62.

[3]) Pharmaceutical Journ. 75 (1905), 861; Chemist and Druggist 67 (1905), 970.

which E. Beckmann and M. Pleissner[1]) named *pulegone*. The properties and derivatives of this substance, which, when pure, boils at 221 to 222°, have been described in vol. I, p. 461.

Other constituents have been ascertained by L. Tétry[2]). The lowest fraction, after repeated distillations over sodium, boiled between 170 and 173° and was strongly lævogyrate. It yielded a bromide melting between 106 and 109°, in all probability a mixture of l-*limonene* and *dipentene* tetrabromide. A nitroso-chloride, m.p. 103°, could not be identified. Of oxygenated constituents, the following were found: *menthol* (about 10 p.c. of the pulegone fraction; m. p. of menthylphenyl urethane 111 to 112°) and *menthone* (m.p. of semicarbazone 184°). The high-boiling fractions contain a deep blue substance *(azulene?)[3])*.

An oil examined by R. Kane[4]) cannot have been a pure pennyroyal oil, neither can a fraction of the boiling point 183 to 185°, the analysis of which agreed with $C_{10}H_{16}O$ or $C_{10}H_{18}O$, have been pulegone.

According to A. Butlerov[5]) Russian pennyroyal oil is distilled from the herb of *Pulegium micranthum,* Claus[6]), a plant that grows in the steppes of southern Russia, more particularly around Sarepta and Astrachan. It has a specific gravity of 0.934. At 202° it begins to distill and boils for the most part at 227°. Its composition corresponds with the formula $C_{10}H_{16}O$. Presumably, therefore it consists principally of pulegone.

Adulteration. Turpentine oil is the most common adulterant. In two instances Schimmel & Co.[7]) observed the addition of eucalyptus oil. This is a rather dangerous adulterant because its presence is not recognized by the odor, also because it alters

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[1]) Liebig's Annalen 262 (1891), 1.

[2]) Bull. Soc. chim. III. 27 (1902), 186.

[3]) Observation made by Schimmel & Co.

[4]) Liebig's Annalen 32 (1839), 286. — Journ. f. prakt. Chem. 15 (1838), 160.

[5]) Jahresber. d. Chem. 1854, 594; Pharmazeut. Zentralbl. 1854, 359.

[6]) According to the Index Kewensis *Pulegium micranthum*, Claus = *Mentha Pulegium,* L. L. Briquet (Engler-Prantl, *Die natürlichen Pflanzenfamilien*) differentiates a variety in southern Russia which he names *Mentha Pulegium,* L. subspec. *micranthum* (Fisch.), Briq.

[7]) Report of Schimmel & Co. November 1908, 81.

the specific gravity and solubility but little. The pulegone content of these oils was only 25 to 30 p.c. instead of 80 p.c. The cineol, which is totally wanting in pure oils, was separated by means of its resorcinol compound.

819. Oil of Peppermint.

Oleum Menthæ Piperitæ. — Pfefferminzöl. — Essence de Menthe Poivrée.

GENERAL.

Origin. The problem of the botanical origin of the peppermint plant and its relation to other species of *Mentha*, one of the most difficult ones of systematic botany, has been solved only but recently. As late as 1891 F. A. Flückiger[1]) designated as peppermint plant a representative of the genus *Mentha* which has the capacity to a high degree, to produce menthol. Now it is known that the plant which yields the peppermint oils of Europe and North America is not a peculiar species but a cross between *Mentha viridis* and *M. aquatica*. It has been designated *Mentha piperita* (L. p. p.), Huds. var. *officinalis,* Sole and of it there exist various groups, subspecies and forms which are cultivated for the production of the oil. They are indicated in connection with the description of the oils distilled in various countries[2]). *Mentha canadensis* var. *piperascens,* Briquet is to be regarded as the parent plant of the Japanese peppermint.

Cultivation. The cultivation of peppermint will be found described in detail in connection with the American (p. 520) and Japanese (p. 531) oils. Here only a few observations and experiences may be mentioned that may stimulate further studies.

First of all mention may be made of the detailed investigations made by H. Thoms in connection with Japanese plants in the botanical garden of the Pharmaceutical Institute at Dahlem[3]). They were later repeated in German Southwest Africa and in East Africa.

[1]) F. A. Flückiger, *Pharmakognosie des Pflanzenreichs.* III. ed. Berlin 1891, p. 723.
[2]) The very complicated botanical relationship has been elucidated by A. Tschirch, Handbuch der Pharmakognosie, vol. 2, p. 921 *et seq.*
[3]) Arbeiten a. d. pharm. Institut der Universität Berlin 8 (1910), 93; 9 (1911), 47; 10 (1912), 75; 11 (1913), 57. — Berichte d. deutsch. pharm. Ges. 20 (1910), 424. — Apotheker Ztg. 26 (1911), 686; 28 (1913), 671.

In the spring of 1909 Thoms obtained a small box of "roots" from a planter in Yamagata-Ken, Japan. The transportation via the Siberian railway had lasted but three weeks, nevertheless a large part of the rhizomes had rotted. In April 1909 the remaining "roots" were set out in the light clay soil of Dahlem and in the course of the summer some of the plants had attained a height of $^3/_4$ m. In August a first distillation could be undertaken which showed that the Dahlem oil was identical with the Japanese oil.

The botanical examination of the plant was undertaken by Briquet, of Geneva, who determined it to be *Mentha canadensis* var. *piperascens,* Briq.[1]).

In the summer of 1910 the distillation was repeated with a larger amount of material. The first distillation was undertaken toward the end of July. A yield of 0.087 to 0.091 p.c. with reference to the fresh plant was obtained, corresponding to a yield of 0.524 to 0.535 computed with reference to the dry material. Judged by the experiences made in Japan a larger yield was to be expected from the harvest in August just before the flowering period. That a smaller yield resulted (0.076 p.c. of the fresh herb, 0.455 p.c. computed with reference to the dry herb) is attributed to the appearance of a rust. This fungus, *Puccinia Menthæ,* Pers. was observed in other parts of Germany during the same summer. On the quantitative composition of the oil this fungus does not seem to have any influence. That this may nevertheless be the case became apparent from a private communication to Professor Thoms by Dr. Sonder who for a number of years has been engaged in the cultivation of peppermint at Oldesloe, a German watering-place. Four thousand of his young plants were infected with *Puccinia Menthæ.* They were not harvested because they were off color and had acquired a very unpleasant odor reminding of *Mentha crispa.* Peculiar to relate, the *Mentha aquatica* growing abundantly in the neighborhood was not affected by this fungus.

Together with the "roots" Thoms had obtained from the Japanese planter mentioned above an oil distilled by himself. Its properties together with those of the German distilled oil are herewith tabulated: —

[1]) Comp. E. M. Holmes, Perfum. Record 4 (1913), 32.

	Japanese Oil	Dahlem Oil (first and second crop)
d	0.8998 (21°)	0.8976 (23°)
$a_{D21°}$	− 36 75°	− 31.85°
Congealing point . .	+ 10 to + 10.5°	+ 8°
A. V.	4.42	2.28
E. V.	22.4	16.2
Menthol as ester . .	6.23 p.c.	4.5 p.c.
Free menthol . . .	73 p.c.	73.4 to 73.7 p.c.
Total menthol . . .	66.7 p.c.	68.9 to 69 p c

Again in the summer of 1911 peppermint oil was distilled from the Japanese plants. The yield, computed with reference to water-free drug was 0.893 p.c. In the mean time "roots" of the Japanese plants had been sent to South Germany, German East Africa; and German Southwest Africa. The latter in particular had thrived. From the dry herb sent to Berlin Thoms obtained 0.862 p.c. of oil computed with reference to water-free drug.

In the following table the properties of the South African oil, the Dahlem oil, and of an oil distilled in Japan are recorded. Noteworthy is the high menthol content of the African product (84.83 p.c.).

	I Older Japanese oil (distilled in Japan)	II Oil of herb from German South- west Africa	III Oil of herb cultivated in Dahlem (Summer 1911)
d	0.9043 (18°)	0.9032 (22°)	0.8954 (22°)
a_D	− 36.25° (23°)	− 35° (24°)	− 34.75° (25.5°)
Congealing point .	could not be determined	+ 20 to 20.5°	+ 14.5°
A. V.	4.05	2.99	4.01
E. V.	27.73	4.68	12.744
Menthol as ester .	7.74 p.c.	1.302 p.c.	3.546 p.c.
Free menthol . .	72.77 p.c.	83.528 p.c.	75.271 p.c.
Total menthol . .	80.51 p.c.	84.830 p.c.	78.817 p.c.

A later communication relates that toward the end of April 1912 roots were planted in the clay soil of Dahlem, that they developed well at first, but that they later suffered from the drought of the spring of 1912 and had to be watered artificially both frequently and freely. The first cut before the flowering period was made July 17, 1912. From 15.8 kg. of air-dried herb 0.74 p.c. of oil were obtained. The second cut was made August 10 and 19.7 kg. of air-dried herb yielded 123 g. = 0.624 p.c. of oil.

The constants of the oils from the first (I) and second (II) cut were as follows:—

I. $d_{15°}$ 0.8987; $\alpha_{D20°}$ — 35.22°; congealing point + 13.5°; menthol as ester 3.78 p.c.; free menthol 75.20 p.c.; total menthol 78.98 p.c.

II. $d_{16°}$ 0.9030; α_D — 35.29°; congealing point + 14.75°; menthol as ester 3.56 p.c.; free menthol 75.65 p.c.; total menthol 79.21 p.c.

On August 20, 1912 the Dahlem Institute received from the Colonial School in Witzenhausen 4.1 kg. of fresh herb raised from "roots" of *Mentha canadensis* var. *piperascens*, Briq. previously obtained from Dahlem. Upon drying there remained 950 g. which yielded upon distillation 8.7 g. = 0.92 p.c. of volatile oil with the following properties: $d_{15°}$ 0.9042; $\alpha_{D20°}$ — 35.295°; menthol as ester 6.99 p.c.; free menthol 74.16 p.c.; total menthol 81.25 p.c.; congealing point + 14.5°.

Finally Thoms reports on a lot of Japanese peppermint cultivated in Okahandja in German Southwest Africa. It was rich in stems. From 45.3 kg. of leaves 555 g. = 1.225 p.c. of oil, and from 24.3 kg. of stems 48.2 g. = 0.2 p.c. of oil were obtained. The leaf oil revealed the following constants: $d_{20°}$ 0.9042; $\alpha_{D20°}$ — 35.29°; menthol as ester 2.31 p.c.; free menthol 83.01 p.c.; total menthol 85.32 p.c.; congealing point + 20.75°.

The oil from the stems showed the following constants: $d_{20°}$ 0.9001; $\alpha_{D20°}$ — 35.3°; menthol as ester 1.71 p.c.; free menthol 82.93 p.c.; total menthol 84.64 p.c.; congealing point + 21°.

By freezing and draining on a force filter the African oil yielded 57.5 p.c. of crude menthol in crystalline form.

Concerning the fungus *Puccinia Menthæ*, previously mentioned, from which English and American peppermint fields suffer considerably, W. Himmelbaur[1]) has made interesting observations. They were made in connection with young plants of *Mentha piperita* (L. *ex parte*), Huds. var. *officinale*, Sole, which were grown in a long narrow bed of an experimental garden in Prague. The location was unfavorable in so far as on the one side it was only 1.5 m. from a high wall and, on the other side was shaded by a tree. Another cultural experiment was made in Korneuburg,

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[1]) Zeitschr. f. d. landwirtsch. Versuchswesen in Österreich 1914, Fascicle 3/4.

Austria, where *Mentha arvensis* f. *piperascens,* Mal. (= *canadensis* f. *piperascens,* Briq.) was planted. The beds were unshaded but in the vicinity of a gas factory. Moreover, the location was very dry and exposed to winds. Toward the beginning of August a weakening of the plants was observed on account of the unfavorable conditions. In Prague damages due to smoke were first observed and later an attack by *Puccinia Menthæ,* in Korneuburg the attack by *Puccinia* came first, then the damage due to smoke. With the aid of numerous illustrations Himmelbaur describes the progress made by the disease. Compared with healthy mint plants it became apparent that the leaves invariably carried drops of a yellow substance and many crystals. The drops consisted of fatty oil, the crystals presumably were hesperidin, a glucoside, found principally in the *Rutaceæ.* Neither of these substances are found normally in large quantities in *Mentha.*

As a first result of the damage here described the production of chlorophyll appears to be reduced. As a further visible result of the deep-seated disturbance an overproduction of such substances as hesperidin or fatty oil takes place. Hesperidin is to be regarded as a waste product of plant metabolism and is never reutilized. Thus the capacity for resistance against damage by smoke and against fungi is diminished. Smoke that passes over plants rapidly does not injure healthy plants.

As the author points out, the peppermint plant is rather particular in regard to locality and condition of soil. It demands a fairly moist, but light and sunny location that is not exposed to winds.

As best remedy against the mint rust B. Pater [1]), who has conducted experimental cultivation of peppermint in Klausenburg, Hungary, recommends the earlier cutting of the plants and not to wait until the appearance of the flowers. In general it is assumed that the plant produces most oil during the flowering period. However, it must be considered that the leaves attacked by the rust are valueless. Apparently the disease spreads from the ground, for the lower leaves are infected first, whence the disease spreads upwards.

[1]) Die Heilpflanzenversuchsanstalt der landwirtschaftlichen Akademie in Kolozsvár. Fascicle 1. Kolozsvár (Klausenburg) 1914.

Pater has also cultivated plants, that were obtained from the gardens of the father Josef Agnelli, of Csári, which he designated *Mentha piperita* var. *Agnelliana*. The drying of the herb was effected naturally as well as artificially in a hop dryer. The naturally dried herb contained 0.7024 p.c., the artificially dried herb 0.8844 p.c. of oil. Plants set out in the spring of 1908 were so weak and degenerate in 1912 that they were of little service. To begin with the soil was poor, which possibly accounts for the failure of the fertilization experiments.

According to Pater about 80 000 "roots" are required to plant a hectare.

That the Japanese plant thrives very well in Hungary becomes apparent from a statement by K. Irk[1]). Roots of *Mentha canadensis* var. *piperascens,* which he had obtained from Berlin-Dahlem in 1911, were propagated with success. The oil distilled from the herb harvested in 1913 had the following properties: $d_{4^\circ}^{25^\circ}$ 0.8968; n_{D25° 1.4606; E. V. 19.6; menthol as ester 5.54 p.c.; free menthol 75.58 p.c.; total menthol 81.12 p.c. The herb raised from seed yielded an oil with α_1, — 34.14° and a total menthol content of 76.01 p.c., thus revealing that the plants raised from seed contain less menthol than those raised from roots.

According to the investigations of F. Pilz[2]) peppermint appears to have a great desire for potash, but is less particular in its demands for phosphoric acid. The leaves are richer in lime, phosphoric acid and nitrogen than the stems, whereas both leaves and stems contain about the same amounts of soda and potash.

Production and Commerce. As to the amount of peppermint oil produced, the producing countries may be considered in the following order: —

Japan. Originally the production of peppermint oil had its seat exclusively in the vicinity of Yonezawa. In recent decades, however, it has also spread to the district of Bingo Bitchiu — both in Hondo — also to Hokkaido (Yezo), the northernmost island. The production districts are indicated on the map in vol. II,

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[1]) Pharm. Zentralh. **55** (1914), 459.

[2]) Zeitschr. f. landw. Versuchswesen in Österreich **15** (1912), 575; Chem. Zentralbl. **1912**, II. 743.

p. 468 on which they are colored. The amounts of oil produced
in 1909 were estimated as follows: —

A (Yamato) . . . .   100 kin[1]
B (Bingo Bitchiu and Bizen)   . . . .   8500 „
C (Sanuki) . . . .   200 „
E (Ischikari, Techio and Tokachi) | 20000 „
H (Kitami) . . . . | (Hokkaido) | 80000 „
N (Shinano). . . . .   300 „
Y (Uzen) . . . .   500 „
                                              ‾‾‾‾‾‾‾‾‾‾‾
                                             109600 kin
                                          = abt. 65900 kg.

Details as to area and yield in the several districts up to
1904 may be consulted in the thesis of Naojiro Inouye[2]) on
"Japanese Peppermint".

The amount of oil produced in recent years has, however,
increased enormously. Thus according to Japanese estimates it
was 850000 kin in 1913 as opposed to 135000 kin in 1909. The
exportations increased hand in hand with the increase in pro-
duction. The following data supply information as to production,
price and export.

Japanese Oil.

Production value of menthol and oil.

1901 . . . 1732983 Yen[3])   1907 . . . 1322772 Yen
1902 .   . 772104 „   1908 . . . 633998 „
1903 .   . 1119403 .   1909 . . . 1340480 „
1904 .   . 2308269 „   1910 . . . 1679851 „
1905 . . . 2183231 „   1911 . . . 2870882 „
1906 . .   2305076 „

Estimates of harvest (approximate data "v" before, "n" after the harvest).

1903   200000 Catties[4]) oil   1909 v. 110000 kin oil
1904   500000 kin   „   1909 n. 135000 „   „
1906 v. 255000   „   „   1910 v. 210000 „   „
1906 n. 195000   „   „   1910 n. 184000 „   „
1907 v. 260000   „   „   1911 v. 200000 „   „
1907 n. 200000   „   „   1911 n. 264000 „   „
1908 v. 170000   „   „   1912 v. 470000 „   „
                                   1913 n. 850000 „   „

[1]) 1 Kin = 601 g.
[2]) Report of Schimmel & Co. November 1908, 199.
[3]) 1 Yen = 2.09 ℳ.
[4]) 1 Catty = 605 g.

Comparative yield of the three cuts in a district.

	1905	1906	
I. Cut	20 000	6 000	kin oil
II. „	70 000	40 000	„ „
III. „	50 000	35 000	„ „

Approximate price in shilling per lb. Engl.

		Oil, dementholized	Menthol
December	1899	4/5	10/3
July	1902	3/3	–
January	1903	13/–	—
July	1903	—	22/–
September	1903	5/– to 5/9	18/–
November	1903	—	15/–
December	1903	4/–	9/–
November	1906	6/3	10/–
Summer	1907	—	8/–
March	1908	4/2	6/–
December	1909	5/10	9/··
March·	1910	5/1	8/3
September	1910	6/–	9/8
April	1911	7/6	16/6
December	1912	—	30/–[1])
April	1913	—	—
December	1913	4/–[2])	9/–[3])

Export.

	Menthol		Oil	
	Kin	Yen	Kin	Yen
1880	—	—	3 726	5 232
1881	--	—	6 928	10 258
1882	---	—	9 940	14 671
1883	—	—	7 166	13 085
1884	--	—	9 017	25 781
1885		---	15 362	45 541
1886	81 018	43 189	60 997	63 207
1887	22 369	25 618	86 423	76 527
1888	13 910	17 657	31 982	33 102
1889	18 221	30 755	36 894	46 310
1890	27 219	71 433	29 362	42 883
1891	16 931	49 660	28 079	39 656
1892	16 689	56 232	18 632	38 207
1893	12 028	54 867	31 802	121 687
1894	21 135	143 108	57 807	242 679

[1]) Computed in. the basis of 20 Yen per Kin.
[2])   „   „   „   „   „ 2,75 „   „   „
[3])   „   „   „   „   „ 6 „   „   „

	Menthol		Oil	
	Kin	Yen	Kin	Yen
1895 . . .	30 826	197 411	31 911	112 911
1896 . . .	60 000	318 657	84 054	234 213
1897 . . .	30 700	124 750	26 800	55 959
1898 . . .	25 500	116 202	19 800	52 043
1899 . . .	45 600	190 424	30 605	73 123
1900 . . .	30 485	172 501	20 836	50 971
1901 . . .	65 394	437 051	55 670	108 237
1902 . . .	54 332	463 719	59 202	164 847
1903 . . .	76 851	804 401 ⎰ highest ⎱ price	77 024	277 617
1904 . . .	144 148	1 090 724	174 769	558 949
1905 . . .	167 067	797 642	173 906	491 591
1906 . . .	95 549	517 215	121 138	371 478
1907 . . .	—	337 865	—	292 706
1908 . . .	55 406	263 937	103 906	199 925
1909 . . .	102 411	490 525	151 801	466 657
1910 . . .	—	648 857	—	—
1911 . . .	114 371[1]	963 220	171 900[2]	624 800[2]
1912 . . .	133 600[3]	1 589 729	185 700[4]	694 700[4]

The principal ports of export of peppermint oil and menthol are Yokohama and Kobe.

Thanks to the excellent steamer connection with Hamburg, this place has developed into the principal European market for Japanese peppermint oil. Second and third are London and New York with considerable intervals. The amounts imported *via* Hamburg are herewith tabulated: —

Imports in Hamburg via the sea route, according to the "Tabellarische Übersichten des Hamburger Handels" in the "Handelsstatistisches Amt".

Peppermint oil.

from	1910	1910 value	1911	1911 value
Japan	58 440 kg.	719 410.— ℳ	61 070 kg.	798 350.— ℳ
United States . .	27 740 ,,	687 460.— ,,	24 690 ,,	671 150.— ,,
China	3 060 ,,	27 520.— ,,	7 210 ,,	51 340.— ,,
Great Britain. . .	9 370 ,,	173 790.— ,,	10 900 ,,	241 020.— ,,
France	600 ,,	6 260.— ,,	430 ,,	4 920.— ,,
Other imports . .	80 ,,	1 850.— ,,	170 ,,	2 750.— ,,
	99 290 kg.	1 616 290.— ℳ	104 470 kg.	1 769 530.— ℳ

[1] 151 538 lbs. Engl. valued at 98 300 £. ⎱ Dipl. and Cons. Rep., London,
[2] 227 800 lbs. Engl. valued at 63 860 £. ⎰   No. 5151 (1913), 13.
[3] 177 000 lbs. Engl. valued at 162 300 £. ⎱ Dipl. and Cons. Rep., London,
[4] 246 000 lbs. Engl. valued at 71 000 £. ⎰   No. 5161 (1913), 45.

from	1912	1912 value	1913	1913 value
Japan	60 750 kg.	869 610.— ℳ	78 810 kg.	1 122 150.— ℳ
Hongkong . . .	4 340 ,,	57 930.— ,,	1 100 ,,	15 500.— ,,
United States . .	16 010 ,,	546 050.— ,,	20 180 ,,	631 610.-- ,,
Great Britain. . .	7 910 ,,	203 160.— ,,	14 110 ,,	297 840.— ·,,
Russia	1 260 ,,	35 000.— ,,	210 ,,	5 530.-- ,,
	92 270 kg.[1])	172 290.-- ℳ[1])	115 750 kg.[1])	2 087 300.— ℳ[1])

Menthol.

from	1910	1910 value	1911	1911 value
Japan	38 220 kg.	673 870.— ℳ	47 500 kg.	1 220 910.— ℳ
United States . .	90 ,,	1 900.— ,,	1 040 ,,	43 180.— ,,
China	—	—	310 ,,	4 100.- ,,
Singapore . . .	140 ,,	1 600.— ,,	·	--
Great Britain . .	5 380 ,,	92 180.— ,,	2 610 ,,	61 990.· ,,
France	—	—	760 ,,	15 400.— ,,
	43 830 kg.	769 550.— ℳ	52 200 kg.	1 345 580.— ℳ

from	1912	1912 value	1913	1913 value
Japan	48 520 kg.	1 955 500.— ℳ	69 310 kg.	3 146 780.— ℳ
Hongkong . . .	500 ,,	15 000.— ,,	—	—
United States . .	--	—	530 ,,	24 210.— ,,
Great Britain. . .	1 150 ,,	54 010.— ,,	2 570 ,,	106 220.— ,,
Bremen	200 ,,	7 300.— ,,	1 370 ,,	38 300.— ,,
	50 790 kg.[1])	2 034 300.— ℳ[1])	73 810 kg.[1])	3 317 100. - ℳ[1])

North America. The principal district lies in the states of Michigan and Indiana. Formerly New York State controlled the market. It was the Wayne County oil — with Lyons as principal center — that was given preference ·over the "western oil" from Michigan. Since about 1911, however, the cultivation of peppermint in Wayne County has been practically abandoned, indeed the peppermint oil industry in New York State has practically ceased to exist. Nevertheless, market reports still continue to quote "Wayne Co. peppermint oil".

The oldest and best known American commercial brands are those of "H. G. Hotchkiss" (H. G. H.), under which crude, natural oil only is sold; and of "F. S. & Co.", under which rectified American peppermint oil has been marketed since 1872.

[1]) These figures for 1912 and 1913 are to be regarded as total imports. The slight differences to be found in the totals are due to the fact that imports from other countries were so small as to be ignored.

Large quantities of crude American oil enter commerce in "tins" or "cans". A very well-known brand is that of A. M. Todd. The principal sales of American peppermint oil are made by New York jobbers, some of whom have permanent purchasing agents in the distillation districts.

Area of cultivation in Michigan:

	1900	1901	1902
Area	2112	2782	6410 acres[1]
Yield of oil .	47628	63718	82420 lbs. Engl.[2]
Per acre . .	22.5	23.9	12.8 " "

Area cultivated:	1905		1906		1907	
	Acres	estimated yield of oil lbs. Engl.	Acres	estimated yield of oil lbs. Engl.	Acres	estimated yield of oil lbs. Engl.
Wayne Co., New York	933	23325	416	17800	646	13265
Michigan	7375	184375	7316	9200	6490	110330
Indiana	1000	25000	1169	12500	1111	36633

Area cultivated:	1908		1909		1910	
	Acres	estimated yield of oil lbs. Engl.	Acres	estimated yield of oil lbs. Engl.	Acres	estimated yield of oil lbs. Engl.
Wayne Co., New York	380	6735	279	5675	56	692
Michigan	8339	—	7498	—	7130	—
Indiana	1118	—	2537	—	3546	—

Area cultivated:	1911		1912		1913	
	Acres	estimated yield of oil lbs. Engl.	Acres	estimated yield of oil lbs. Engl.	Acres	estimated yield of oil lbs. Engl.
Wayne Co., New York	20	307	—	—	—	—
Michigan	7392	—	8600	—	8393	—
Indiana	3983	.	4596	—	6518	.

Area cultivated:	1914		1915	
	Acres	estimated yield of oil lbs. Engl.	Acres	estimated yield of oil lbs. Engl.
Wayne Co., New York	—	—		
Michigan	8921 }	550000 to	10434 }	?
Indiana	10090 }	600000	12158 }	?

Oil yield (estimated) in lbs. Engl.

1905	1906	1907	1908	1909	1910	1911
232700	122330	160228	—	—	200000	240000

[1] 1 acre = 40.4 *Ar.*
[2] 1 lb. Engl. = 453.6 g.

Production according to the official Census for 1909.

Fiscal year[1])	1899/1900	1904/05
Peppermint oil	202 550 lbs. valued at $ 188 509	130 022 lbs. valued at $ 470 037

Fiscal year[1])	1909/10
Peppermint oil	305 781 lbs. valued at $ 519 079
of this crude	269 081 „ „ „ „ 450 981 (abt. 88 p.c.)
„ „ refined	36 700 „ „ „ „ 68 098 („ 12 p.c.)
„ „ from Michigan .	227 521 „ „ „ „ 382 613 („ 75 p.c.)
„ „ „ other states	78 260 „ „ „ „ 136 466 („ 25 p.c.)

Approximate prices per lb. Engl.

October 1890 . . . . $ 2.50	October 1901 . . . $ 1.30
„ 1891 . . . . „ 2.70	„ 1902 . . . „ 2.—
„ 1892 . . . . „ 3.—	March 1903 . . . „ 5.—
„ 1893 . . . . „ 2.80	October 1903 . . . „ 3.—
„ 1894 . . . . „ 2.20	„ 1905 . . . „ 2.50
„ 1895 . . . . „ 2.—	„ 1906 . . . „ 3.—
„ 1896 . . . . „ 1.70	April 1908 . . . „ 2.—
„ 1897 . . . . „ 1.80	October 1910 . . . „ 2.—
„ 1898 . . . . „ 1.—	April 1911 . . . „ 3.—
„ 1899 . . . . „ 0.80	1912 at first rising, then declining
„ 1900 . . . . „ 0.90	October 1913 . . . $ 3.50

Export.

1892/93 . . . $ 54 987	1898/99 . . . $ 145 375
1893/94 . . . „ 99 629	1899/00 . . . „ 117 462
1894/95 . . . „ 80 225	1900/01 . . . „ 89 558
1895/96 . . . „ 87 633	1901/02 . . . „ 60 166
1896/97 . . . „ 85 290	1902/03 . . . —
1897/98 . . . „ 162 492	

				of this to Germany	
1903/04	—		—		
1904/05	36 953 lbs. valued at $ 135 060		27 210 lbs. valued at $ 102 694		
1905/06	74 151 „ „ „ „ 206 261		35 855 „ „ „ „ 99 464		
1906/07	147 722 „ „ „ „ 499 082		61 785 „ „ „ „ 209 967		
1907/08	141 617 „ „ „ „ 357 555		58 532 „ „ „ „ 156 987		
1908/09	161 811 „ „ „ „ 288 318		57 310 „ „ „ „ 118 023		
1909/10	—	„ 215 845	—		—
1910/11	—	„ 269 034	—		—
1911/12	—	„ 422 631	—		—
1912/13	—	„ 395 551	—		—
1913 Y'y—Dec.	—	„ 249 060.	—		—

[1]) The fiscal year is from July 1 to June 30.

England. Statistical data as to the oil harvests do no exist. As to the principal places of distillation, area of cultivation and estimates as to yields see p. 541. A few figures revealing the price development of Mitcham oil, as the English oil is commonly designated in commerce, are herewith given:—

		Price of crude oil in sh. per lb. Engl.	of the rectified oil in ℳ per kg.
April	1900 . . .	—	61.50
Fall	1902 . . .	26/- to 30/-	64.— to 70.—
„	1903 . . .	32/-	76.—
„	1906 . . .	34/-	—
„	1907 . . .	34/- to 36/-	80.—
„	1908 . . .	31/-	—
„	1909 . . .	30/- to 31/-	—
„	1910 . . .	27/-	—
„	1911 . . .	34/- to 35/-	80.—
„	1912 . . .	30/- to 32/-	—
„	1913 . . .	31/- to 32/-	—

In *France* and *Italy* the cultivation of peppermint, more particularly of Mitcham plants, has increased from year to year. Italy has even begun to export oil, whereas until a few years ago the production sufficed merely to cover the own demands. Importation was checked by high duties. Thus in 1913 Italy is reported to have exported 2 229 500 kg. oil valued at 1 092 455 Lire. The industry is located exclusively in the *Département des Alpes-Maritimes* and in the provinces of Turin and Piemont.

In *Germany* the production of peppermint oil has gone backward during recent decades and in Thuringia has ceased almost altogether. From the poorer drug, not suitable for medicinal purposes, cured from the herb raised in Cölleda, Ringleben and other Thuringian communities only a poorer grade of oil is obtained. On the other hand the cultivation of peppermint on a large scale has been started in the vicinity of Leipzig. A distillation outfit with modern apparatus in the very midst of the fields, yields an oil of superior quality that has been purified by special methods. However, the annual production has not exceeded 600 kg. thus far. The oil distilled in limited quantities in Gnadenfrei, Silesia, is also one of the best oils.

Properties. As already pointed out, the plants yielding the peppermint oils in different parts of the globe are not a single

botanical species, variety, or form. Hence, it will be readily understood that the several oils differ greatly as to their properties and composition. For practical purposes odor and taste are controlling factors, properties by which the expert is able to differentiate the principal kinds of commercial oil. This is of importance because of the great difference in price. Unfortunately, the origin of an oil cannot always be ascertained by a chemical and physical examination. It is for the most part impossible in the case of mixtures.

Peppermint oil is colorless, yellowish or greenish in color, of an agreeable, refreshing odor and a cooling, persistent taste. It is rather limpid, but with age becomes darker and more viscid.

OIL FROM DRY AND OIL FROM FRESH HERB. Appreciable differences are shown by oils as to whether they have been distilled from fresh herb or from dry herb. The latter is mostly the case. Distillation of fresh herb has, first of all, the disadvantage that it requires more time than that of dry or wilted herb. In addition readily resinifiable substances pass over into the oil which during the drying of the herb are oxidized to non-volatile resins and are thus rendered harmless. This same resinification process is undergone by the oils which have been distilled from fresh herb; their specific gravity increases and their solubility in 70 p.c. alcohol is diminished or lost, as was shown by the investigation made by Schimmel & Co.[1]) in Barrême, southern France.

Two oils distilled from fresh herb were examined two weeks after distillation when they revealed the following properties: —

1. d_{15^o} 0.9184; α_D — 10° 44'; menthol as ester 12.0 p.c.; total menthol 50.2 p.c.
2. d_{15^o} 0.9273; α_D — 10° 56';   „   „   „   14.8 „ ;   „   „   54.7 „

When the density was redetermined after 14 days an appreciable increase was observed. The following observations at intervals of 14 days showed additional increases: —

	Original	After 14 days	After 4 weeks	After 6 weeks
1. d_{15^o}	0.9184	0.9191	0.9224	0.9292
2. d_{15^o}	0.9273	0.9291	0.9322	0.9380

SEPARATION OF MENTHOL IN THE COLD. The normal Japanese oil is so rich in menthol that even at ordinary temperature it

[1]) Report of Schimmel & Co. April 1909, 77.

congeals to a solid mass saturated with oil. In connection with the best oils, however, it is necessary for them to remain in the freezing mixture for some length of time before crystallization begins. Hence the amount of menthol that crystallizes out is no criterion of the quality of the oil.

COLOR REACTIONS. Peppermint oil reveals various color reactions of which those produced by acids are the most beautiful and striking. If in a test tube 5 drops of peppermint oil and 1 cc. of glacial acetic acid be mixed, a blue color results upon several hours' standing, the intensity of which increases gradually until the maximum has been reached after 24 hours. In connection with certain oils the mixture reveals a deep blue color toward transmitted light, whereas reflected light shows a copper-colored fluorescence. In connection with English oils this phenomenon is less intense, frequently only a light blue color with a slightly reddish fluorescence appears. Japanese oil[1]) does not give this reaction, the mixture remains colorless.

Gentle heating accelerates the reaction greatly. However, the resulting color is not as pure a blue, but more violet. For the success of the reaction access of air is necessary. If the air be excluded no color reaction becomes perceptible even after several days. Hence the change is to be regarded as an oxidation phenomenon. The reaction can be brought about very quickly if 2 cc. of oil, 1 cc. glacial acetic acid and 1 drop of nitric acid are mixed. In this case even the Japanese oil assumes a slight violet coloration.

According to E. Polenske[2]) the cause of this reaction is to be sought in a nitrogen-free, volatile substance found in the oil. The pigments which this substance yields with acids reveal a characteristic spectroscopic behavior. The substance itself is decomposed by light, for an oil that has been exposed to sunlight for some time no longer gives the color reaction.

Another color phenomenon is produced if a solution of 1 cc. of oil in 5 cc. alcohol is heated with 0.5 g. sugar and 1 cc.

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[1]) F. A. Flückiger, Pharmaceutical Journ. III. 1 (1871), 682 and III. 2 (1871), 321.

[2]) Arbeiten a. d. Kaiserl. Ges. Amt, Berlin 6 (1890), 522. — Pharm. Ztg. 35 (1890), 547.

hydrochloric acid. The mixture acquires a deep blue, violet, or bluish-green coloration[1]).

A red or light brown color is obtained when chloral hydrate and hydrochloric acid are added to peppermint oil[2]).

Although the several peppermint oils show a different behavior toward these and other[3]) color reactions the various shades of color are not differentiated sufficiently to distinguish the various kinds of oil. An English journal[4]) is of the opinion that the coloration stands in no relation to the ester content of the oil, as has been assumed. In general it must be admitted that the cause of the formation of these color phenomena is no more known than the composition of the substances producing them.

Composition. *Menthol* is the characteristic constituent of all peppermint oils. On account of its capacity for crystallization it was early recognized[5]). It has been investigated repeatedly by older and more recent chemists. Properties and chemical derivatives of this interesting substance have been described in vol. I, p. 387. For the most part menthol occurs free in peppermint oil and only in small part as *acetate* and *valerate*.

In addition to the crystallizable menthol, the oil contains its isomers, presumably such as are of a determining influence on the quality of the oil. That of the theoretically numerous isomeric menthols only a single one, *viz.* the *neomenthol*[6]), has been isolated from the Japanese oil finds its explanation in the difficulty with which these closely related compounds are separated. *Menthone* is another constituent which all peppermint oils have in common. Apparently it was first isolated by G. H. Beckett and A. Wright[7]).

The more recent chemical investigations restrict themselves to an oil of definite origin. Inasmuch as the varying peculiarities of the oils depend on the chemical composition of these oils, the results ascertained in connection with one oil should not necessarily be ascribed to another oil. For this reason the

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[1]) A. Ihl, Chem. Ztg. 13 (1889), 264.

[2]) C. Jehn, Arch. der Pharm. 208 (1873), 29 and 205 (1874), 326.

[3]) Concerning the color reactions produced with citric acid and paraformaldehyde see p. 511.

[4]) Perfum. Record 4 (1913), 33.

[5]) Comp. vol. I, p. 192.

[6]) See p. 538.

[7]) Journ. Chem. Soc. 14 (1876), 1; Jahresber. d. Chem. 1876, 397.

statements concerning the chemical composition of the oils are restricted to the description of the several oils.

Examination. The physical constants of peppermint oil should first be determined, special attention being given to the question of solubility. Important also is the determination of menthol, both free and as ester, as first suggested by F. B. Power and C. Kleber[1]) and described in vol. I, p. 575.

According to the U. S. Pharmacopœia VIII the esterified and total menthol in peppermint oil are determined together by saponifying quantitatively 10 g. of oil and acetylating after repeated washing with water. G. Heikel[2]) points out that, according to circumstances, much menthol may be lost when operating thus, indicating too low a menthol content. Because of the saponification the relative solubility of the components of the oil are changed and the washing of the saponified oil results in a removal of menthol as was demonstrated experimentally by Heikel. Thus, an oil which contained a total menthol content of 51.6 p.c. when assayed according to the U. S. P. VIII showed only 19.6 p. c. In order to avoid such errors, Heikel suggests the acetylation of the unsaponified oil and to determine the ester content separately.

During the process of acetylation it is necessary to provide for adequate condensation of the vapors otherwise ester will escape and thus be lost to the assay[3]).

The menthone content is determined according to the method described in vol. I, p. 590.

As adulterants of peppermint oil the following substances have been observed: — acetines (the acetic esters of glycerin)[4]), copaiva balsam[5]), cedar wood oil[6]), petroleum[7]), mineral oil[8]) and camphor oil[9]).

[1]) Pharm. Rundsch. (New York) 12 (1894), 162.

[2]) Americ. Journ. Pharm. 80 (1908), 373.

[3]) Journ. ind. eng. Chemistry 6 (1914), 40J; Report of Schimmel & Co. April 1915, 33.

[4]) Chemist and Druggist 62 (1903), 591.

[5]) *Ibidem* 63 (1903), 154.

[6]) *Ibidem* 64 (1904), 854.

[7]) *Ibidem* 72 (1908), 770.

[8]) Report of Schimmel & Co. April 1903, 59. — Chemist and Druggist 61 (1902), 948.

[9]) Report of Schimmel & Co. April 1908, 59. — Chemist and Druggist 61 (1902), 520.

American Peppermint Oil.

Origin. The peppermint oil distilled from the peppermint plant and its varieties is one of the principal oils produced in the United States. Three kinds of mint, according to A. Henkel [1], are cultivated, the so-called American mint (*Mentha piperita,* L.) and two varieties, the black mint (*Mentha piperita vulgaris,* Sole) and white mint (*Mentha piperita officinalis,* Sole) [1]. These presumably correspond to *M. piperita* var. *officinalis* forma *rubescens,* Camus and forma *pallescens,* Camus of the new nomenclature.

American mint has become indigenous in many of the eastern states from the New England States to Minnesota and south to Florida and Tennessee. The black mint is hardier and yields better than the other two kinds, hence is cultivated on practically all of the peppermint farms. The white mint yields a very fine oil but on account of its sensitiveness and the small yield is cultivated but little [1].

Cultivation and Distillation. The ground is plowed in fall and disced during the next spring. Into furrows, three feet apart [2]), the roots, $1/4$ in. thick and 1 to 3 ft. long are placed so as to form a continuous line. These "roots" are the runners of the previous year. A skilled laborer can plant $1/2$ to 1 acre in a day. After several weeks the ground is gone over with a horse cultivator and then carefully gone over with the hoe in order to remove all weeds. By June new rhizomes have been produced which by August and September cover the ground like a network. These are used during the next year for new cultures. The harvest begins in the second half of August when the long purple inflorescences begin to appear. The crop from the fields of the previous year is harvested first. Having been cut, the peppermint is allowed to wilt, however, the drying is not carried so far as to cause the leaves to drop. Then it is distilled as soon as possible. Some distillers distill the green plant fearing the loss of oil during drying. This fear is unfounded. Moreover, the practice has the

[1] Alice Henkel, Peppermint. U. S. Dept. of Agricult., Bureau of Plant Industry, Bull. No. 90, Part III. Washington 1905.

[2] A. M. Todd, The American Peppermint Industry. V. Internat. Congress of applied Chemistry 1903. Report vol. 2, p. 804. — Chemist and Druggist **68** (1903), 482. — Perfum. Record 1 (1910), 7; 5 (1914), 252.
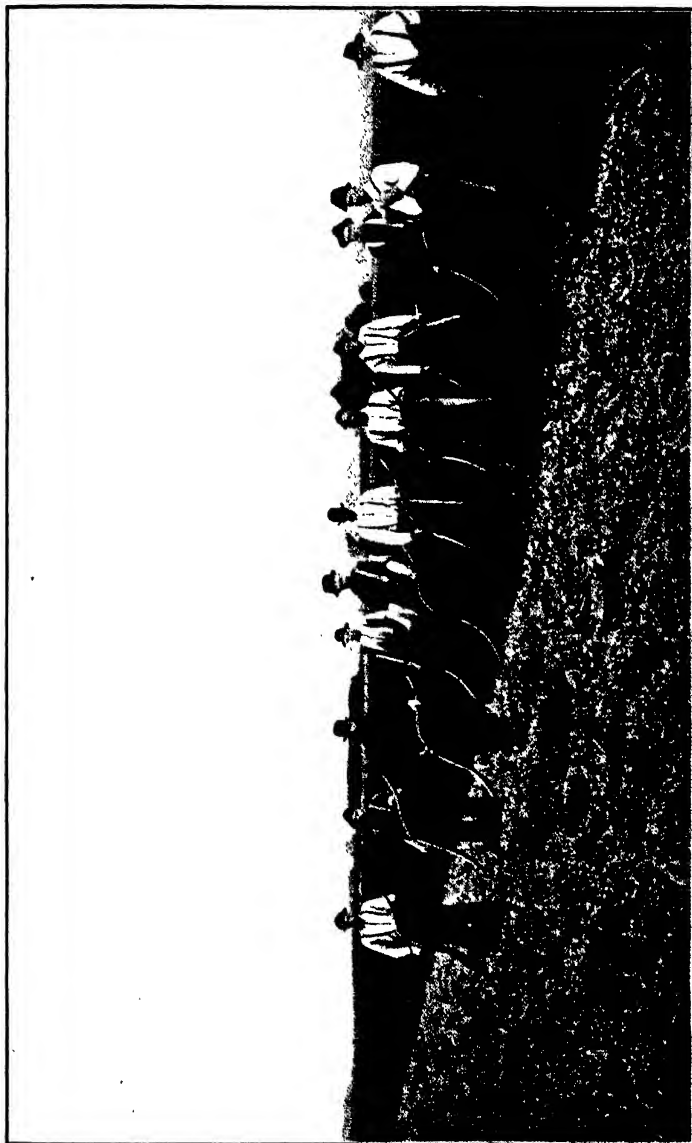
Fig. 40.   Peppermint harvest in Michigan.

disadvantage that the distillation requires again as long[1]). The distillation of a charge of well-dried herb lasts 30 to 40 minutes, whereas a charge of green herb moistened by rain requires 2 hours.

For a long time the distillation of peppermint oil in the United States of North America was conducted with simple copper stills . over direct fire. In 1846 some of the larger farmers and distillers began the distillation with steam from large wooden vats, after
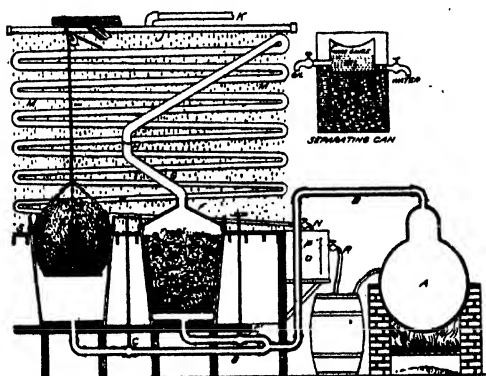
Fig. 41. Peppermint distillation.

(According to Dewey, in Baileys Cyclopedia of American Horticulture.)

A Boiler. B Steam pipe. C, C' Steam valves. D Herb in the still ready for distillation. E Removal of exhausted.herb. F Removable top which is used alternately for both stills. G Movable pipe leading to condenser. J Sprinkler supplying water to cool condensor tubes M. N Exit of mixture of oil and water. O and P Water and oil in receiver. R Water overflow.

it had been demonstrated that all conditions were favorable for the development of the industry.

With the older stills but 15 lbs. of oil could, at best, be obtained from a charge. Steam distillation from wooden apparatus enables the distillation of from 75 to 100 lbs. of oil at a time without appreciable extra expense.

At the present time several styles of equipment are in use. All of them, however, consist of a boiler, two wooden vats, a cooler and a receiver. The vats are the stills proper and alter-

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[1]) Comp. also Proceed. Americ. Pharm. Ass. 84 (1886), 121. — Americ. Druggist Sept. 1886, p. 161 and June 1888. — Proceed. N. Y. State Pharm. Assoc. 1888. — Pharmaceutical Journ. III. 19 (1888), 3, 4.
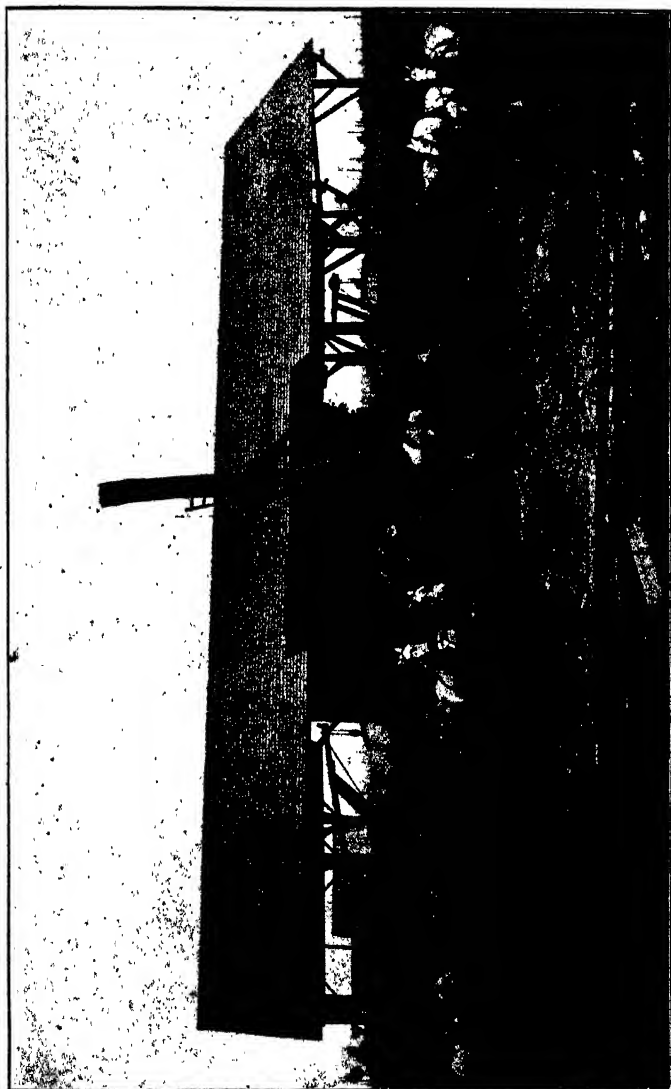
Fig. 42. American peppermint oil still.

nately receive the herb and are discharged. They are 6 ft. high and have a diameter of 5 ft. A steam pipe passes from the boiler under the false bottom of the vat so that the steam passes through the charge from below. In the larger distilleries the vats have a capacity of from 2000 to 3000 lbs. of dry herb.

The herb rests on a false bottom which is provided with chains with the aid of which bottom and exhausted charge can be removed as shown in fig. 41. The charging is effected by having one man pitch the herb into the still whereas another tramps it down. By injecting a little steam from time to time the herb is moistened and thus admits of firmer packing. The still having been sealed, steam is passed through the mass of herb from below until it is exhausted.

The yield from dry herb fluctuates between 0.1 and 1 p.c. For an average of 10 years Todd obtained 0.3 to 0.4 p.c.

The frequently observed poor condition of American peppermint oil was due to the fact that other labiates and even composites[1]) were distilled with the peppermint, more particularly *Erigeron canadensis*, L., *Erechthites hieracifolia*, Raf., *Hedeoma pulegioides*, L., also *Ambrosia* (ragweed) species. This evil has been removed in recent years by more careful cultivation and weeding of the fields.

The production of peppermint oil in the United States made its beginning in 1816 in Wayne Co., in the northwestern part of the State of New York. For a longer period it was conducted on a small scale by individuals in neighboring counties as well. In 1835 the cultivation of peppermint was introduced into Michigan, first into St. Joseph County. This industry has spread more and more between the Ohio River and Lakes Erie, Huron and Michigan[2]).

At the present moment Michigan is the principal state among the peppermint oil-producing states. In Wayne County, N. Y., the production of oil has diminished greatly and scarcely any peppermint is now cultivated[3]).

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[1]) F. Stearns, Proceed. Americ. Pharm. Ass. 7 (1858), 449 to 459. — J. M. Maisch, Americ. Journ. Pharm. 42 (1870), 120; Arch. der Pharm. 192 (1870), 252.

[2]) A. M. Todd, Proc. Americ. Pharm. Ass. 34 (1886), 121.

[3]) Report of Schimmel & Co. October 1918, 81. — See also p. 512.
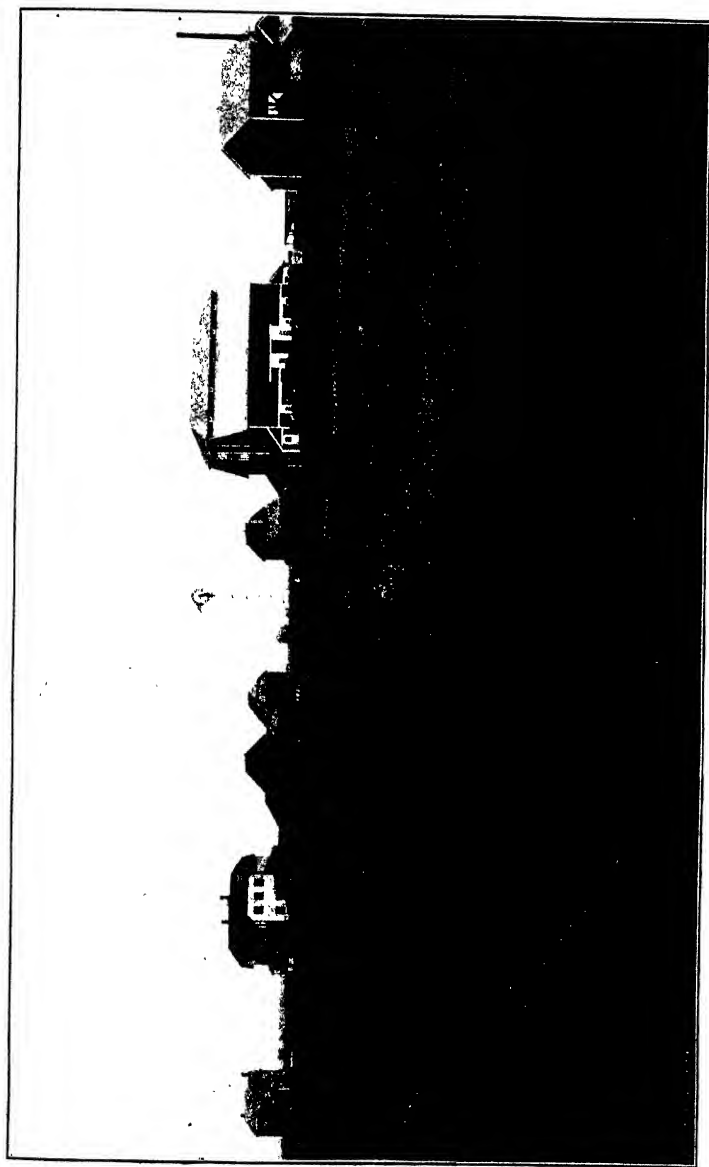
Fig. 43. Campania farm of A. M. Todd, near Kalamazoo, Michigan.

Composition. A very detailed investigation of the constituents of American peppermint oil has been made by F. B. Power and C. Kleber[1]). The oil was distilled from Wayne Co. herb from which all weeds had been carefully removed. The yield amounted to 0.67 p.c.; d_{15}. 0.9140; α_D — 32°0'; menthol as ester 14.12 p.c.; free menthol 45.5 p.c.; total menthol 59.6 p.c. Distilled in a fractionating flask 2.6 p.c. passed over below 200°, 2.4 p.c. between 200 and 205°, 8.6 p.c. between 205 and 210°; 18.8 p.c. between 210 to 215°; 24 p.c. between 215 to 220°, 19.6 p.c. between 220 and 225°, 9 p.c. between 225 to 230°, and 3.6 p.c. between 230 and 235°, leaving a residue of 12.2 p.c. On account of the great care with which the plant material had been sorted and because of the more perfect distillation facilities, the oil had a much more pleasant odor than the ordinary oil of commerce.

Not less than 17 different, well characterized individual substances have been identified in American peppermint oil up to the present time.

It contains: —

1. Acetaldehyde, about 0.044 p.c., yielded acetic acid upon oxidation.
2. Isovaleric aldehyde, about 0.048 p.c. (b. p. 92°, yielded valeric acid upon oxidation).
3. Free acetic acid.
4. Free isovaleric acid.
5. α-Pinene[2]), inactive, possibly a mixture of d- and l-α-pinene (pinene nitrolpiperidine, m. p. 118°; pinene nitrolbenzylamine, m. p. 123°).
6. Phellandrene (nitrite, m. p. 100°).
7. Cineol (cineol hydrobromide, cineolic acid, m. p. 196°).
8. l-Limonene (tetrabromide, m. p. 104°).
9. Menthone (conversion into menthol).
10. Menthol, b. p. 215.5°.
11. Menthyl acetate.
12. Menthyl isovalerate.

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[1]) On the constituents of American Peppermint Oil and a method for the quantitative determination of Menthol. Pharm. Rundsch. (New York) 12 (1894), 157. — Über die Bestandteile des amerikanischen Pfefferminzöls. Arch. der Pharm. 232 (1894), 639.

[2]) Report of Schimmel & Co. April 1894, 41.
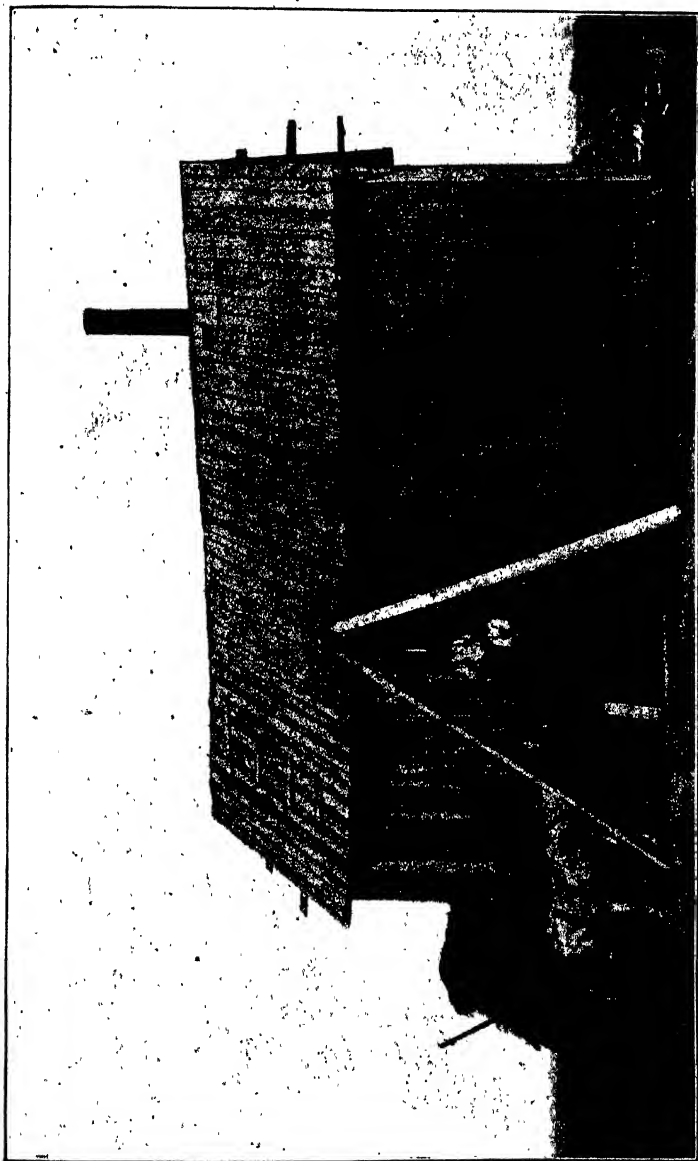
Fig. 44. Distillation of peppermint in Decatur, Michigan.

13. Menthylester of an acid $C_8H_{12}O_2$.

14. A lactone $C_{10}H_{16}O_2$, m. p. 23°, of a stale odor reminding of borneol. The corresponding hydroxyacid crystallizes from petroleum ether in shining needles that melt at 93°.

15. Cadinene[1]) (dihydrochloride, m. p. 118°).

16. Amyl alcohol[2]) (acetate).

17. Dimethyl sulphide[3]).

In addition, higher boiling, decomposable sulphur compounds appear to be present in American peppermint oil. It not infrequently happens that during the rectification of the oil a very penetrating odor reminding of rotting turnips becomes apparent towards the middle of the distillation.

In order to prove the presence of dimethyl sulphide in peppermint oil 1 ccm. is distilled from 50 ccm. of the crude oil, and the distillate superposed over an aqueous solution of mercuric chloride. After a short time the formation of a white film will be observed at the zone of contact. On account of its volatility the dimethyl sulphide accumulates in the first fraction during rectification, hence rectified oils from which the lowest fractions have been removed no longer give this reaction.

Menthene, $C_{10}H_{18}$, b. p. 158 to 160°, which according to G. Andres and A. Andreef[4]), is said to occur in Russian peppermint oil, could not be found in the American oil in spite of all attempts to find it. Equally futile were the attempts to find a terpene $C_{10}H_{16}$ boiling at 175° and possessing the properties of Brühl's[5]) so-called menthene.

Properties. $d_{15°}$ 0.900 to 0.915; α_D —18 to —34°; $n_{D20°}$ 1.460 to 1.463; menthol as ester 5 to 9 p.c.; total menthol 48 to 63 p.c.; menthone 9 to 16 p.c., rarely higher, up to 25 p.c.; soluble in 2.5 to 5 vol. of 70 p.c. alcohol, occasionally with slight opalescence which increases with greater dilution.

As to the menthone content, it would seem that the plants produce larger amounts of this ketone in the earlier stages of

[1]) First observed by Hälsey (Proceed. Wisc. Pharm. Ass. 1898, 90).

[2]) Report of Schimmel & Co. April 1894, 41.

[3]) *Ibidem* October 1896, 58.

[4]) Berl. Berichte 25 (1892), 609.

[5]) *Ibidem* 21 (1888), 157.

development and that later part thereof is reduced to menthol. At least an observation by C. Kleber[1]) suggests this possibility which, however, requires further supplementation. In the following table the oils are arranged in the order in which they were received in New York during the season of 1913. Inasmuch as the oils were delivered directly from the stills, the order of the series possibly corresponds fairly accurately with the order of production.

No.	Received	$d_{25°}$	α_D	Total menthol	Menthone
I	21. August	0.8995	25° 27'	49.7 p.c.	18.8 p.c.
II	3. September	0.8983	− 24° 20'	48.4 „	16.8 „
III	10. „	0.900	- 24° 14'	51.7 „	17.98 „
IV	10. „	0.904	24° 28'	50.2 „	16.98 „
V	10. „	0.902	24° 3C'	50.2 „	17.7 „
VI	10. October	0.905	23° 18'	53.5 „	14.0 „
VII	10. „	0.901	− 26° 12'	56.1 „	13.9 „
VIII	11. „	0.902	-- 25° 30'	55.8 „	16.7 „
IX	20. „	0.903	-- 23° 49'	56.4 „	15.2 „

The optical rotation is much the same as usual and the specific gravity of the earliest oils is slightly lighter. The menthol content, however, of these oils is relatively low and in part does not attain the pharmacopœial minimum of 50 p.c. On the other hand the menthone content exceeds the normal. In the October deliveries, however, the oils showed a perfectly normal behavior, disregarding a slightly increased menthone content. In all probability these observations were due to abnormal harvest conditions which compelled the producers to distill imperfectly developed herb.

The Wayne Co. oils, which have disappeared almost entirely from the market (see p. 512 and 524), had the following properties: $d_{15°}$ 0.910 to 0.920; α_D − 25 to − 33°; menthol as ester 8 to 14 p.c.; total menthol 50 to 60 p.c.; menthone content about 12 p.c.; the oil did not dissolve to a clear solution in 70 p.c. alcohol, but in $^1/_2$ vol. and more of 90 p.c. alcohol.

JAPANESE PEPPERMINT OIL.

Origin. As already stated, H. Thoms in 1909 obtained roots of Japanese peppermint plants from Yamagata-Ken, which were planted in Dahlem near Berlin and which thrived there. According

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[1]) Report of Schimmel & Co. April 1914, 77.

to the botanical determination made by J. Briquet, of Geneva, the parent plant is to be regarded as *Mentha canadensis* var. *piperascens*, Briq.[1]). Briquet is of the opinion that it is the same species which Holmes had designated as *Mentha arvensis*, D.C. var. *piperascens*, Holmes[2]). According to English[3]) opinion, however, these examinations dealt with two species. Thus, the plant which was examined by Holmes and at the same time by the French botanist Malinvaud, was recognized by both as a variety of *Mentha arvensis* and showed distinct differences from the species examined by Briquet. Naojiro Inouye[4]), in his comprehensive monograph on Japanese peppermint, points out that, according to Nagasaki[5]), the present plant, of which four cultural varieties are known, is the product of numerous improvements.

1. *Akamaru* (from *aka* — red and *maru* — round). The leaves are round and the stems purplish, the flowers pale violet. The oil and menthol content are larger than in the other varieties.
2. *Aomaru* (from *ao* = green and *maru*). Leaves round, stems blue and flowers pale violet.
3. *Akayanagi* (from *aka* and *yanagi* — willow). The willow-like leaf is of pale violet color on the lower surface, the stem is blue, the flowers are white. The oil content is low.
4. *Aoyanagi*. Leaves willow-shaped, stems blue, flowers white. Resembles the wild plant.

The first of these four varieties is regarded as the best.

Inasmuch as the results of the investigations by Holmes and Briquet do not harmonize, the differences may possible be explained by assuming that these botanists had two of these varieties under consideration.

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[1]) H. Thoms, Berichte d. deutsch. pharm. Ges. 20 (1910), 424. — Arbeiten aus dem Pharm. Institut d. Univers. Berlin 8 (1911), 93. An illustration of the plant is to be found in vol. 10, p. 76.

[2]) Pharmaceutical Journ. III. 13 (1882), 381.

[3]) Perfum. Record 4 (1913), 32.

[4]) Naojiro Inouye, Japanese Peppermint. From the Laboratory of Prof. Edward Kremers, Madison, Wisconsin. Supplement to Report of Schimmel & Co. November 1908, 205.

[5]) Yamagata = *Sonderbericht der landwirtschaftlichen Versuchsstation.* No. 4: *Die Kultur der Pfefferminze im Bezirk* Yamagata. Published by the Experimental. Station of the Division for Agriculture and Commerce. February 1899 (2. ed. March 1901).

Distribution of Peppermint Cultivation. Whereas only a few years ago the cultivation of peppermint was restricted to Hondo, the principal one of the Japanese islands, the more northern island Hokkaido (Yezo) has, since 1906, outstripped all other sections[1]. In Hokkaido the first peppermint gardens were planted by immigrants from the Yamagata district (Hondo). The province of Kitami is the principal oil producing district in Hokkaido and in it Notsuke-Ushi (Tokora) and Yubetsua (Monbetsu) are the principal centres[2].

Cultivation. According to Nagasaki[3]) the Japanese peppermint once planted, being a perennial, can be kept from five to seven years. For two to three years after the planting the oil yield is greatest and then gradually becomes less. As a rule the gardens are replanted after four or five years. It is better still to sow wheat or barley, or to plant certain beans before replanting with peppermint. Such a cycle, especially with leguminous plants, yields the best results.

The propagation is not effected by seeds, which bring about a deterioration of the plant, but by means of runners, which are planted in spring or mostly in fall. The plants that are to be used for transplanting are marked in the field. Either the entire field is ploughed and the roots of the marked plants are collected, or the marked plants are dug up separately. For propagation the Akamaru variety is selected, but it is impossible to exclude other varieties. While it is true that this variety is superior to others, its vitality has been diminished by long periods of cultivation so that it is crowded out by the stronger varieties, *e. g.* Aoyanagi. This is the reason why most of the fields show different varieties. This phenomenon is least observed in the Yamagata district.

In transplanting, the old runners, which break when bent, are discarded and only the young, succulent white "roots" are selected and are cut into pieces 4 to 5 in. long. After the

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[1]) Yeinosuke Shinosaki, Journ. ind. eng. Chemistry 5 (1913), 656; Report of Schimmel & Co. October 1913, 83.

[2]) Comp. the map of Japan inserted in vol. II between pp. 468 and 469. This map, however, is still divided into the old *kuni* and not into the modern districts (prefectures or *ken*).

[3]) According to Inouye, *loc. cit.*

ground has been ploughed and otherwise prepared, these sections of roots are planted in furrows 14 to 16 inches apart.

Fall planting is carried on from the end of October to the end of November, spring planting from the end of March to the first of May. Special care is given to good fertilizer and to the removal of weeds.

According to the district, the herb is harvested once, twice or three times[1]). The best oil is produced in the districts of Okayama and Hiroshima (Hondo) where the plant is cut three times, namely in May, June, and August. The oil from the first cut yields 47 p.c. of crystallizable menthol[2]), the second about 53 p.c. and the third about 60 p.c. In the Yamagata district (Hondo) only two cuts are harvested and in Hokkaido but one. But the area cultivated in this district is much greater than in the other districts. Hence, although the oil yields only 45 p.c. of crystallizable menthol, more than half of the total menthol is produced in Hokkaido province.

Having been cut, the herb is tied into bundles and spread out to dry in suitable places. Unless this be done fermentation sets in resulting in the loss of oil. Having been dried, the herb is again tied into bundles which are suspended on the northern sides of the houses where they are protected against direct sunshine, wind, rain and frost. In summer the drying requires ten days, in fall about thirty days.

Distillation. The apparatus in which the distillation of peppermint oil is conducted in Japan differ greatly. Each district seems to have its preferences for a different arrangement. All, however, are rather primitive and untouched by the achievements of modern technology.

Such an equipment is described in detail by E. Marx[3]). The still consists of a broad-rimmed cast iron kettle (*A, I, H,* fig. 45), wooden vats *(B)* and cooler *(C)*. As a rule three of these are arranged in a battery supplied with a common fire-

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[1]) Shinosaki, *loc. cit.*

[2]) This is the menthol that separates upon simple freezing without fractionation.

[3]) Communications on the distillation of peppermint oil in Japan, in Mitteil. d. deutschen Gesell. für Natur- und Völkerkunde Ostasiens 6 (1896), 355.

place. The operation consists in first filling the kettles A, I, H with water. Then the vats (B) with their perforated bottoms are placed in position, are filled with dry herb and provided with straw rings and soft clay as seal. Thereupon the inverse conical condensers C are placed on top of the vats and the fire is started at F. The water vapors laden with oil condense
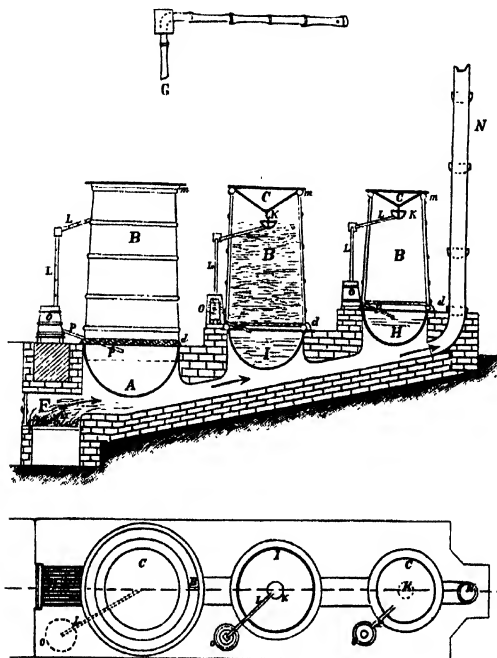
Fig. 45. Japanese peppermint still.

on the inner surface of the inverted cones C and collect in the suspended cup K, whence the condensed water and oil mixture is conducted by means of a bamboo tube L to the receiver O. The water which has separated from the oil flows back into the kettles A, I, and H through the small tube P and thus replaces in part the vaporized water. As soon as the water used for cooling in C has become hot it is withdrawn by means of the bamboo siphon (G).

It is said to occur that the straw rings on the kettles are overheated occasionally and that an empyreumatic odor is thus imparted to the oil. This odor is indeed frequently met with in Japanese peppermint oil.

As becomes apparent from the monograph by Inouye, repeatedly referred to, the stills mounted in a battery of three as illustrated in fig. 45 are also used individually. A better kind of apparatus provided with an
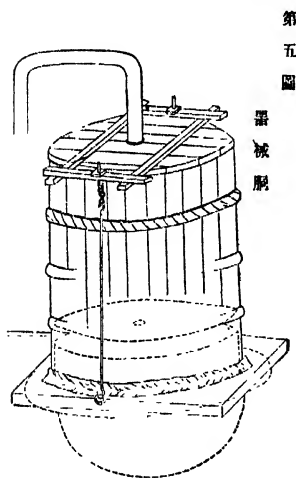
Fig. 46. Improved peppermint still.   Fig. 47. Improved condenser.
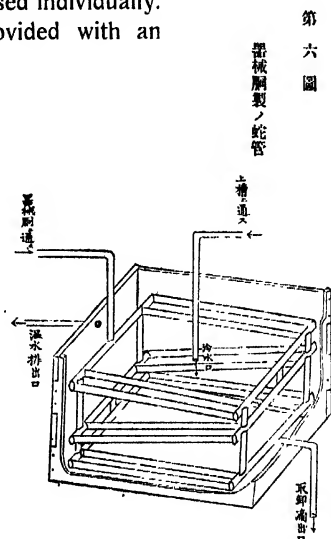
improved condenser is illustrated in fig. 46. Kettle and vat are like those previously described but the inverted conical condenser is replaced by a regular top that is screwed down. The vapors are passed into a special condenser illustrated in fig. 47.

The points of entrance and exit of both condensation water and of vapor and condensed vapor respectively, are indicated by arrows.

Fig. 48 illustrates the arrangement of two such stills with their condensers in the factory of Sato in Hiroshima.

Other distilling apparatus are described by Inouye, also by T. Asahina[1]) (with illustration), and Shinosaki[2]). As a rule the

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[1]) J. E. Gerock, Journ. d. Pharm. f. Elsaß-Lothringen 28 (1896), 314.
[2]) Loc. cit.

distillation of a charge lasts four hours. The yield from the first cut amounts to 1.07 p.c., that of the second 1.83 p.c. and that of the third 1.6 p.c. These values naturally fluctuate and depend on both quality and dryness of the leaves. The second

導荷製建場器械裝置

備候園蘆三郡服部村佐藤農聚油場撮影

Fig. 48. A battery of two stills and two condensers in the factory of Sato.

cut gives the best yield. Thus a field yielded 300 lbs. on the first cut, 800 lbs. on the second, and 600 lbs. on the third. An acre yields about 5000 lbs. of dry leaves which in turn yield about 80 lbs. (1.60 p.c.) of oil[1]).

[1]) Board of Trade Journal 79 (1912), 78; Report of Schimmel & Co. April 1913, 80.

Separation of Menthol. The crude distillate which contains all of the menthol [1]) is called *torioroshi* by the Japanese. This is transferred to tin cans which, as shown in fig. 49 are provided with an exit tube. Four of these tin cans are placed into a refrigerator and surrounded by a freezing mixture of ice or snow and salt (see fig. 50). If after three days a larger amount of menthol has crystallized out, the exit tubes are opened so that for two days the oil may drop into an empty can. The cans containing the menthol are then removed from the freezing mixture and so mounted on a rack that the tubes point downward (fig. 51) when the draining is allowed to continue at room temperature for another two or three days. With the use of the refrigerator the separation of menthol can be accomplished during any season of the year. Most distillers, however, effect it during the colder season. When the menthol separates under the influence of natural cold it rises to the surface and is removed by means of a sieve. From the *torioroshi* an average of 40 to 50 p.c. of menthol are separated.

第七圖

米澤市中村太治郎
分離器

漆山村多納亀五郎
分離器

分離油分受器

Fig. 49. Tin cans for the separation of menthol.

The menthol thus obtained is remelted and congealed and by means of draining freed as much as possible from contaminating oil.

The shipment of menthol, also of dementholized oil ("oil") is effected in 5 lb. tin cans, 12 cans being packed in a box.

Composition. Japanese peppermint oil was examined in 1876 by G. H. Beckett and A. Wright [2]). In the oil that remained after

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[1]) The production of "peppermint camphor" is described in the introduction of M. Moriya's dissertation which was submitted to the University of Tokio in 1880. However, this part of the dissertation was not published. (See also Journ. Chem. Soc. 39 (1881), 77; Jahresber. d. Chem. 1881, 629.

[2]) Journ. Chem. Soc. 1876, I. 3; Jahresber. d. Chem. 1876, 397.

the *menthol* had been separated by refrigeration, they found a substance $C_{10}H_{18}O$ in fraction 210 to 215° which was isomeric with borneol and which may have been *menthone*. In fraction 245 to 255° they suspected a substance $C_{30}H_{50}O$ which, according to their opinion, had resulted by condensation of three molecules of the compound $C_{10}H_{18}O$.

$$3C_{10}H_{18}O = C_{30}H_{50}O + 2H_2O.$$
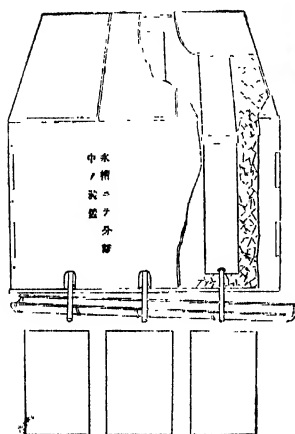
Fig. 50. Arrangement of cans in the refrigerator.
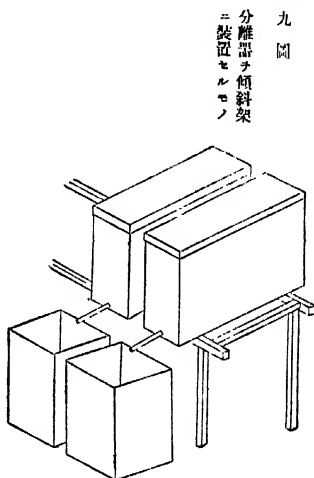
Fig. 51. Draining of the oil after the removal of the cans from the freezing mixture.

Inasmuch as this reaction is not very probable it may be assumed that fraction 245 to 255° consisted of impure *sesquiterpene* mixed with menthol.

Of terpenes the oil contains l-*limonene*. Its tetrabromide melting at 104 to 105° was prepared by Y. Murayama[1] from a fraction with $[\alpha]_D$ — 58.51°, and by Schimmel & Co.[2] from a fraction with α_D — 84° 27'. Phellandrene could not be detected[1].

In the lowest fraction Schimmel & Co.[2] found an alcohol that was recognized as *ethyl*-n-*amyl carbinol*. A fraction

[1] Yakugakuzasshi **307** (1910), 141; Journ. de Pharm. et Chim. VII. 1 (1910), 549.

[2] Report of Schimmel & Co. April 1912, 103.

with the properties $d_{15°}$ 0.8521; α_D — 52° 26'; $n_{D20°}$ 1.45991, was treated with phthalic acid anhydride. The alcohol regenerated from the phthalate had the following properties: b. p. 56 (3.5 mm.); $d_{15°}$ 0.8279; α_D + 6° 17'; $n_{D20°}$ 1.42775. After distillation under diminished pressure its properties had scarcely been altered; b. p. 178.5 to 179.5°; $d_{15°}$ 0.8276; α_D + 6° 26'; $n_{D20°}$ 1.42755. The α-naphthyl urethane of this alcohol melts at 81 to 82°. Upon oxidation with sodium bichromate and sulphuric acid a ketone resulted that reacted with bisulphite. The compound regenerated from the semicarbazone (m. p. 117°) had the following properties; b. p. 170°; $d_{15°}$ 0.8255; α_D + 0° 22'; $n_{D20°}$ 1.41556. Aside from a slight optical activity which may have been due to a slight impurity, this ketone had the constants of ethyl-n-amyl ketone (m. p. of semicarbazone 117 to 117.5°). Thus it was shown that the oil contains d-ethyl-n-amyl carbinol, $C_2H_5CH(OH)C_5H_{11}$.

Further oxidation with sodium bichromate and sulphuric acid yielded n-capronic acid.

A comparison with the synthetic ethyl-n-amyl carbinol, prepared by Schimmel & Co.[1] from n-capronic aldehyde and ethyl magnesium iodide, confirmed the identity of both.

In addition to the common l-menthol, Japanese peppermint oil contains a very small amount of an isomer which had been named *neomenthol* by its discoverers. R. H. Pickard and W. O. Littlebury[2] had obtained from Schimmel & Co. a fraction of Japanese peppermint oil from which the menthol had been separated as completely as possible. After the lowest and highest fractions had been removed it was heated with an equal amount of benzoyl chloride. The reaction being completed, the hydrogen chloride was removed by shaking the mixture with soda solution and menthone and other volatile substances were removed by steam distillation. The esters remaining yielded upon fractionation a mixture of alcohols, from which a fraction with the following properties was obtained: m. p. 80 to 82° (4 mm.); $d_{15°}$ 0.9032; α_D — 8° 48'; menthol content about 90 p.c.

[1] Report of Schimmel & Co. April 1913, 82. Later R. H. Pickard and J. Kenyon (Journ. Chem. Soc. 103 [1913], 1923) described still another method of synthesising ethyl-n-amyl carbinol.

[2] Journ. Chem. Soc. 101 (1912), 109.

This menthol fraction was converted into the acid phthalate that melted at 140 to 143° with $[\alpha]_D + 4.58°$. The ester was recrystallized 28 times from 95 p.c. acetic acid when it melted at 141 to 144°, whereas the optical rotation (in chloroform solution) was $+ 57.16°$. Mixed with d-neomenthylphthalic ester acid this ester melted at 142 to 144°. The alcohol regenerated from the ester yielded l-menthone ($[\alpha_D] - 28.33°$) when oxidized with Beckmann's chromic acid mixture.

Pickard and Littlebury had previously obtained neomenthol, in addition to hexahydrothymol, when they reduced thymol according to the method of Sabatier and Senderens. A comparison of this alcohol with the natural one revealed their identity.

Δ^1-Menthenone[1]) is another, though unimportant constituent. Schimmel & Co.[2]) isolated the ketone by means of its sulphite derivative from the solution of which all compounds not combined with the sodium sulphite had been removed by shaking with ether. The ketone was then liberated by means of caustic potassa. The crude ketone obtained in this manner had the following properties: p.b. 101 to 103° (7.5 mm.); $d_{15°}$ 0.9387; $\alpha_D + 0°30'$; $n_{D20°}$ 1.48675. The ketone purified by repeated fractionation showed the following properties: b. p. 235 to 237° (752 mm.); $d_{15°}$ 0.9382; $d_{20°}$ 0.9343; $\alpha_D + 1°30'$; $n_{D20°}$ 1.48441; mol. refr. found 46.58, computed for $C_{10}H_{16}O/1$ 45.82.

The semicarbazone exists in two modifications. The α-modification melts at 224 to 226°. It is difficultly soluble in alcohol and hence can be purified by boiling with absolute alcohol which removed the readily soluble β-compound. The β-modification, which is more difficult to purify, melts at 171 to 172°.

With hydroxylamine the ketone yields a normal oxime also an oxaminoxime. The oxime is obtained by using the calculated amount of hydroxylamine. However, inasmuch as even under these conditions, some oxaminoxime is found, it is necessary to free the oxime from adhering oxaminoxime by distillation with steam. Recrystallized from alcohol it melts at 107 to 109°.

The oxaminoxime which crystallizes in stubby crystals melts at 164 to 165°. It results readily when an excess of

[1]) O. Wallach, Liebig's Annalen 362 (1908), 272.
[2]) Report of Schimmel & Co. October 1910, 99.

hydroxylamine is employed and can readily be separated from the ketone and its oxime because of its sparing volatility.

When dehydrated with phosphoric acid anhydride Δ^1-menthenone yields cymene, and oxidation with ferric chloride in glacial acetic acid yields thymol. All of the reactions which Δ^1-menthenone is known to give were repeated with the natural ketone.

Properties. At ordinary temperature the normal oil is a crystalline mass saturated with oil. In commerce the normal oil (unseparated), the crystalline mass of crude menthol ("crystals") and the oil separated from these crystals ("oil") are to be found.

The Japanese is the cheapest of all peppermint oils, but on account of its bitter taste cannot be used for all purposes.

NORMAL OIL. $d_{24°}$ 0.895 to 0.902 ($= d_{15°}$ 0.901 to 0.909); congealing point $+ 17$ to $+ 28°$; $\alpha_D - 29$ to $- 42°$; $n_{D20°}$ 1.460 to 1.462; A. V. up to 2; menthol as ester 3 to 6 p.c.; total menthol 69 to 91 p.c.; menthone (one determination) 21.5 p.c.; soluble in 2.5 to 3 vol. and more of 70 p.c. alcohol, the diluted solution occasionally showing opalescence.

LIQUID OIL. $d_{15°}$ 0.895 to 0.905; $\alpha_D - 25$ to $- 35°$; $n_{D20°}$ 1.459 to 1.463; A. V. up to 2.0; menthol as ester 4 to 15 p.c.; total menthol 47 to 68 p.c. in most cases 49 to 55 p.c.; menthone 21 to 30 p.c.; soluble in 2.5 to 4 vol. and more of 70 p.c. alcohol, the diluted solution opalescing for the most part.

In order to distinguish Japanese peppermint oil from other oils a new method has been suggested in addition to the color reaction with glacial acetic acid described on p. 517[1]): A mixture of 1 cc. of oil and 0.5 g of a mixture of equal parts of paraformaldehyde and citric acid is heated on a water bath. The Japanese oil reveals no color change, whereas a purple color results with American, English, Italian and Saxon peppermint oils. This method is preferable to the color reaction with concentrated glacial acetic acid because it is more readily carried out.

ENGLISH OR MITCHAM PEPPERMINT OIL.

Origin. In England two kinds peppermint are cultivated, the "white" mint which has a green stem and the "black" mint which

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[1]) Perfum. Record 2 (1911), 275.

has a purplish stem. According to the recent investigations of
A. and E. G. Camus[1]), the latter is to be regarded as *Mentha
piperita* var. *officinalis* forma *rubescens,* Camus, the former as
M. piperita var. *officinalis* forma *pallescens,* Camus.

Cultivation. In England the cultivation of peppermint is con-
ducted along similar lines as in North America and Japan[2]).
Here also the plant is propagated by roots not by seeds. After
the land has been prepared in winter the plants are set in May.
They are allowed to remain four to five years, though they
afford the best yield in the second year. After the fourth or
fifth year the land has become unsuited for mint cultivation[3]).
But one harvest is gathered annually and it begins about the
third week in August. The herb is spread out on mats so that
it may dry partially before it is transferred to the still.

The areas of cultivation and distillation of peppermint are
located in the Counties of Kent, Surrey, Hertfordshire, Suffolk,
Cambridgeshire and Lincolnshire in the vicinity of Mitcham,
Maddon, West Croydon, Wallington, Carshalton, Ewell, Dorking,
Leatherhead, Caterham, Chelsfield, Long Melford, Elsenham,
Hitchin and Market Deeping. The total area of the Mitcham
district is estimated at 450 to 500 acres, about 50 acres being
cultivated with the "white" mint which is preferred. The total
oil production of the districts enumerated is estimated at 20000 lbs.
Statistics do not exist.

Distillation. In part the old stills, heated with direct fire
are still in use, for the most part, however, large steam stills
are now employed which have a capacity of $^1/_2$ to $1^1/_2$ tons of
herb[4]). The distillation of a charge requires, as a rule, 5 hours,
but the bulk of the oil passes over during the first two hours.

One acre yields 4 to 6 tons of herb and the ton yields $2^1/_2$
to 6 lbs. of oil. The statements as to yield of oil per acre fluctuate

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[1]) Berichte von Roure-Bertrand Fils October 1911, 3.

[2]) Concerning the cultivation of English Peppermint comp. The Chemist's
and Druggist's Diary 1908, 237; Umney, Perfum. Record 1 (1910), 292; W. A. Bush,
Americ. Perfumer 8 (1913), 122.

[3]) Journal of the Board of Agriculture 15 (1908), No. 5; Report of Schimmel
& Co. October 1909, 97.

[4]) Comp. J. C. Shears, Perfum. Record 1 (1910), 96.

between 10 and 30 lbs. According to H. J. Henderson [1]), the plants which grow in open, sunny places give much more oil than those which grow in moist, shady places. The former yielded 0.409 p.c. of oil from fresh herb, the latter but 0.1 p.c.

Properties. English peppermint oil, mostly referred to as Mitcham oil, is highly esteemed on account of its fine aroma and taste. Inasmuch as other countries now produce equally good oils, the English oil has lost its former dominant position. $d_{15°}$ 0.901 to 0.912; α_D — 21 to — 33°; $n_{D20°}$ 1.460 to 1.463; A. V. up to 1.6; menthol as ester 3 to 21 p.c. (3 to 8 p.c. for the oils from "white" mint and 13 to 21 p.c. for the oils from "black" mint); total menthol 48.5 to 68 p.c.; menthone 9 to 12 p.c. (only a few determinations!); soluble in 2 to 3.5 vol. and more of 70 p.c. alcohol; the diluted solution opalescent in individual cases and even turbid.

Composition. From English peppermint oil F. A. Flückiger and F. B. Power [2]) isolated two lævogyrate terpenes boiling between 165 and 170° (mixtures of pinene and phellandrene?) and 173 to 176° respectively (mixture of phellandrene and limonene?), also a dextrogyrate sesquiterpene (probably cadinene) boiling between 255 and 260°. J. C. Umney [3]) proved the presence of *phellandrene* by means of the nitrite reaction and showed that the acids combined with menthol are *acetic* and iso*valeric* acids as in the American oil. There can be no doubt but that most of the substances isolated from American peppermint oil will, upon careful examination, also be found in the English oil.

<center>FRENCH PEPPERMINT OIL.</center>

Origin and Production. In France peppermint is cultivated for the production of oil in the Département Alpes-Maritimes in the vicinity of Grasses, Cannes, Vence, Cagnes and Villeneuve-Loubet, which is regarded as the principal centre [4]); furthermore in the Département Basses-Alpes about Entrevaux, Barrême and Castellane, in Var near Fayence, and in Haute-Garonne near

[1]) Chemist and Druggist **79** (1911), 216.

[2]) Pharmaceutical Journ. III. **11** (1880), 220. — Arch. der Pharm. **218** (1881), 222.

[3]) Pharmaceutical Journ. **56** (1896), 123 and **57** (1896), 103.

[4]) Berichte von Roure-Bertrand Fils October 1906, 34.

Revel on the Montagne noir. Cultivations of some importance are also found in Vaucluse. Whereas in England the hectare produces but 11 to 17 kg. of oil, the same area in France is said to yield 50 kg. of oil[1]). On the average 400 kg. of herb yield 1 kg. of oil or 0.25 p.c.[2]) The black or red peppermint yields even 0.33 p.c.[3]) In Grasse alone 4000 to 5000 kg. of oil are produced annually[4]). In Vaucluse the cultivated areas cover 250 to 300 hectares[5]). In Revel 60000 kg. of herb are distilled annually[1]).

Apparently the cultivation of English peppermint is now quite generally given preference. At Grasse Roure-Bertrand Fils[6]) cultivate the "white" mint, *Mentha piperita,* Huds. var. *officinalis,* Sole forma *pallescens,* Camus, also the "black" or red mint, *M. piperita,* Huds. var. *officinalis,* Sole forma *rubescens,* Camus, whereas in Vaucluse[5]) the latter only is cultivated.

Directions for French peppermint cultivation, which was originally restricted to the Grasse district but which later extended in the Var valley to Entrevaux, are given by L. Belle[7]), also by A. Rolet[8]), professor at the horticultural school in Antibes.

As has been shown by E. Charabot and C. Ebray[9]), also by M. Molliard[10]), the *Menthe basiliquée* is a degenerated peppermint plant produced by an animal parasite, the *Eryophyes Menthæ,* Molliard. It is accompanied by a serious deterioration of the oil.

The development of the oil in the plant has been studied by E. Charabot and A. Hébert[11]). They have investigated the influence of sodium chloride, sodium nitrate, and other salts on the growth of the plant[12]).

[1]) Perfum. Record 2 (1911), 13; 5 (1914), 7.

[2]) Berichte von Roure-Bertrand Fils October 1902, 38.

[3]) *Ibidem* October 1911, 40.

[4]) *Ibidem* October 1907, 44.

[5]) Perfum. Record 1 (1910), 294.

[6]) Berichte von Roure-Bertrand Fils October 1911, 11.

[7]) Journ. Parfum. et Savonn. 20 (1907), 80; Report of Schimmel & Co. October 1907, 74.

[8]) Parfum. moderne 7 (1914), 73.

[9]) Bull. Soc. chim. III. 19 (1898), 117.

[10]) Berichte von Roure-Bertrand Fils October 1905, 3.

[11]) Compt. rend. 130 (1900), 257, 518; 138 (1904), 380.

[12]) Compt. rend. 132 (1901), 159; 134 (1902), 181, 1228; 136 (1903), 160, 1009, 1678. — Bull. Soc. chim. III. 27 (1902), 204, 914; 29 (1903), 612, 698.

Composition. Upon fractionation of the saponified French oil Roure-Bertrand Fils [1]) isolated and identified the following constituents. 1. Iso*valeric aldehyde* (m. p. of ammonia compound 56 to 58°). 2. Iso*amyl alcohol* (b. p. 132°, oxidation to *iso*valeric aldehyde). Whether the alcohol is present free or as ester has not been ascertained. 3. l-α-*Pinene* (b.p. about 155°, m.p. of nitrosochloride 102 to 103°). 4. Δ^3-p-*menthene* (not definitely determined). 5. *Cineol.* 6. l-*Menthol.* 7. d-*Menthone.* According to an earlier communication by the same firm [2]) the oil contained *acetic acid* and *valeric acid esters.*

Properties[3]). $d_{15°}$ 0.910 to 0.927; α_D — 5 to — 35°; $n_{D20°}$ 1.462 to 1.471; A. V. up to 1; menthol as ester 4 to 21 p.c.; total menthol 45 to 70 p.c.; soluble in 1 to 1.5 vol. of 80 p.c. alcohol, the addition of more solvent causing opalescence and even turbidity. Some oils are soluble in 3.5 vol. of 70 p.c. alcohol.

Hand in hand with diseased external changes such as those of the sting of the insect producing the *Menthe basiliquée* (see above), changes in the properties and composition of the oil have been observed. The specific gravity increases, the lævorotation changes to dextrorotation, and the menthol content sinks appreciably. $d_{15°}$ 0.924 to 0.935; α_D + 4 to + 7°; n_{D20} 1.471 to 1.473; menthol as ester 8 to 11 p.c.; total menthol 40 to 42 p.c.

	Ordinary peppermint		Red peppermint	
$d_{15°}$	0.9191	0.9184	0.9170	0.9136
α_D	— 10° 54'	— 8° 2'	— 16° 38'	— 13° 44'
Solubility in 80 p.c. alcohol	1 vol., followed by turbidity	—	1 vol., followed by turbidity	—
A. V.	0.8	0.8	1.0	1.2
E. V.	40.5	31.7	18.9	17.5
Menthyl acetate . .	14.3 p.c.	11.2 p.c.	6.7 p.c.	6.2 p.c.
E.V. after acetylation	160.8	169.1	180.2	185.6
Total Menthol . . .	50.9 p.c.	53.9 p.c.	58.0 p.c.	60.0 p.c.
Free Menthol . . .	39.6 p.c.	45.1 p.c.	52.8 p.c.	55.1 p.c.
Menthone content .	7.3 p.c.	—	16.8 p.c.	—

[1]) Berichte von Roure-Bertrand Fils April 1909, 40.

[2]) *Ibidem* March 1900, 17. — Bull. Soc. chim. III. 19 (1898), 117.

[3]) Comp. also Report of Schimmel & Co. April 1905, 62; October 1906, 58 and Berichte von Roure-Bertrand Fils October 1908, 23; October 1909, 14.

The properties of two different varieties that are cultivated in southern France have been determined by Roure-Bertrand Fils[1]). What is to be understood by "common peppermint" does not become quite apparent. The "red" peppermint in question is *Mentha piperita*, Huds. var. *officinalis* forma *rubescens*, Camus.

From dry peppermint leaves *(Mentha piperita)* that had dropped during the growth of the plant, J. Muraour[2]) obtained a yellow oil with a yield of 0.4 to 0.5 p.c. Its odor reminded of that of Japanese peppermint oil and it showed the following constants: —

	Sample I	Sample II
$d_{15°}$	0.913	0.911
α_D	$- 38°18'$	$- 40°4'$
Menthyl-acetate	33.16 p.c.	40.31 p.c.
Total menthol	43.99 p.c.	45.67 p.c.
	Sol. in 1.5 vol.	Sol. in 2.5 vol.
	80 p c. alcohol.	80 p.c. alcohol.

The limit values given by Muraour in his contribution are much too narrow and hence not applicable. The conclusions therefore drawn from the properties of this oil sample examined by him are not warranted.

ITALIAN PEPPERMINT OIL.

Origin and Production. Whereas formerly peppermint of indefinite origin was and, in fact, even today is being cultivated, since some time English Mitcham mint, both the "white"[3]) and "black"[4]) varieties are now being cultivated in various places, e. g. in Pancalieri in Piemont. The yield from fresh herb amounts to 0.02[3]) to 0.025 p.c.[4]). In 1910 4000 kg.[3]), according to another statement 10000 kg. of Italian Mitcham oil, as it is called to differentiate it from Piedmont oil from old plants, is said to have been distilled. 1 ha. of Italian Mitcham plants are said to yield 50 kg. of oil, whereas the hectare of indigenous plants yields but 30 kg.[4]). 350 kg. constitute a charge, the fresh flowering herb resting on a grating. The distillation is con-

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[1]) Berichte von Roure-Bertrand Fils October 1911, 39.
[2]) Bull. Soc. chim. IV. 9 (1911), 66.
[3]) W. S. Flick, Perfum. Record 2 (1911), 136.
[4]) Parfum. moderne 3 (1911), 116.

ducted either with steam[1]) or over direct fire[2]). An attempt to cultivate English peppermint plants in Messina was soon given up[3]).

Properties[4]). d_{15}. 0.909 to 0.926; α_D — 2° 30′ to — 26° 51′; $n_{D20°}$ 1.462 to 1.468; A. V. up to 0.6; menthol as ester 3.3 to 10.4 p.c.; total menthol 44 to 67 p.c.; menthone 8 to 21 p.c. As a rule the oils form a clear solution with 3 to 7 vol. of 70 p.c. alcohol, additional solvent causing opalescence and even turbidity. In a few instances 70 p.c. alcohol would not yield a clear solution.

The oil of the above-mentioned peppermint cultivated in Messina has been examined by J. C. Umney and C. T. Bennett[5]). Noteworthy is the difference in the oils distilled at different times. The oil (yield 0.4 p.c.) from the first (July) cut had the following properties: d 0.908 and 0.906; α_D —14 and —21°; total menthol 40 and 41.6 p.c.; free menthol 36.2 and 36.9 p.c.; ester computed as menthyl acetate 4.8 and 6.0 p.c.; soluble in 3 vol. of 70 p.c. alcohol. The oil from the second (December) cut had the following properties: d 0.920; α_D —23°; total menthol 70.5 p.c.; free menthol 47.4 p.c.; ester 29.4 p.c.; insoluble in 70 p.c. alcohol, soluble in 2 vol. and more of 80 p.c. alcohol.

GERMAN PEPPERMINT OIL.

Saxon peppermint oil is not surpassed by any of the commercial varieties as to delicacy of aroma and taste. It is the highest-priced of all peppermint oils. Inasmuch as the annual production amounts to but several hundred kilos it is no important factor in the world's market. $d_{15°}$ 0.900 to 0.915; α_D —23 to —37°; $n_{D20°}$ 1.458 to 1.469; A. V. up to 1.3; menthol as ester 2.8 to 20.8 p.c.; total menthol 48 to 81 p.c.; menthone 12 to 23 p.c.; soluble in 2.5 to 5 vol. and more of 70 p.c. alcohol, the diluted solution being turbid at times.

The peppermint oil distilled in limited amounts in Gnadenfrei, Silesia, is one of the best oils and closely resembles the Saxon oil.

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[1]) W. S. Flick, Perfum. Record **2** (1911), 136.

[2]) Parfum. moderne **3** (1911), 116.

[3]) Perfum. Record **2** (1911), 13.

[4]) Comp. also footnotes 1 and 2, also L. Bourdet, Bull. Sciences pharmacol. **18** (1911), 392.

[5]) Chemist and Druggist **66** (1905), 945; **67** (1905), 970.

The oil which is distilled in Cölleda, Ringleben (Thuringia) and other places from the waste of peppermint unsuited for purposes as drug, yields mostly an inferior oil of an unpleasant odor reminding somewhat of spearmint. $d_{15°}$ 0.899 to 0.930; α_D —27 to —34°. With 70 p.c. alcohol the oil, as a rule, does not yield a clear solution.

RUSSIAN PEPPERMINT OIL.

Origin. The Russian oil no more enters the world market than do the French, Italian and German oils of peppermint, for it is mostly consumed in the domestic market. It is produced in the Government Tambov[1]), in the Caucasus[2]), and in the Ukraine[3]), principally in the Government Poltava[4]), where the annual production is estimated at 9000 kg.

As stated by J. Maisit[5]), English "black" mint is cultivated at an altitude of about 500 m. in the Sotchi district on the Black Sea in Caucasia. The oil is distilled in new modern apparatus. From the dry flowering herb a yield of about 1.6 to 1.7 p.c. of crude oil is obtained.

Properties. $d_{15°}$ 0.904 to 0.920; α_D —17 to —26°; menthol as ester 3 to 11 p.c.; total menthol 50 to 58 p.c.; menthone (one determination) 16.35 p.c.; for for the most part soluble in 70 p.c. alcohol. Two oils distilled in the Caucasus had the following properties[5]): —

Oil from	$d_{20°}$	α_D	A. V.	Menthol as ester	Free menthol	Total menthol
1 year old plants	0.912	—17°42'	0.57	6.57 p.c.	42.44 p.c.	49.01 p.c.
2 year old plants	0.913	—17°57'	0.56	8.74 p.c.	41.33 p.c.	50.07 p.c.

Composition. A Russian oil distilled in the Government Kasan has been examined by G. Andres and A. Andreef[6]). In addition to *menthol* they found a dextrogyrate *menthone,* probably a

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[1]) J. Schindelmeiser, Apotheker Ztg. 21 (1906), 927.

[2]) J. Maisit, Arch. der Pharm. 249 (1911), 637.

[3]) Perfum. Record 5 (1914), 314.

[4]) Zeitschr. f. angew. Chem. 28 (1915), III. 517.

[5]) J. Maisit, Arch. der Pharm. 249 (1911), 637.

[6]) Berl. Berichte 25 (1892), 609. — G. Andres, Pharm. Zeitschr. f. Rußl. 29 (1890), 341.

mixture of both isomers·in which the dextrogyrate modification predominated. The analysis of fraction 158 to 160° yielded results that indicated a mixture of a hydrocarbon $C_{10}H_{18}$ with a terpene (pinene?). The authors, therefore, assume the presence of a *menthene* which, however, they did not isolate in the pure state. Fractions 173 to 175° contained l-*limonene* (m.p. of tetrabromide 102°; m.p. of nitrosochloride 103°; m.p. of dihydrochloride 49.5 to 50°).

In an oil obtained from the Government Tambov, J. Schindelmeiser[1]) proved the presence of i-*α-pinene* (m.p. of nitrosochloride 103°; m.p. of nitrolpiperidide 118°), *dipentene* (m.p. of tetrabromide 125 to 126°; m.p. of nitrosochloride 103°; m.p. of carvoxime 92 to 93°), *cineol*.(m.p. of hydrogen bromide derivative 57°), a mixture of l- *and* d-*menthone* in which the lævogyrate modification predominated, and finally *menthol* and its *acetic* and *valeric* *esters*. Neither phellandrene nor menthene, the presence of which was claimed by Andres and Andreef, was found.

DALMATIAN PEPPERMINT OIL.

Schimmel & Co.[2]) have investigated a number of peppermint oils which had been distilled by J. Giaconi, of Trieste, from French peppermint plants cultivated in Dalmatia. Most of the oils had been distilled from fresh herb. Some were crude oils, others rectified. The crude oils had a peculiar odor reminding of pennyroyal. Apparently this can be removed by rectification for the rectified oils no longer possessed this peculiarity. Hence the rectified oils might be considered for the production of liquors and perfumes. The constants of these oils fluctuated between the following limits: —

	Crude oils	Rectified oils
$d_{15°}$	0.9074 to 0.9127	0.9094 to 0.9141
$α_D$	— 15°45′ to —20°58′.	— 11°45′ to — 18″12′
$n_{D20°}$	1.46229 to 1.46684	1.46041 to 1.46783
A. V.	0 to 1.9	0 to 1.0
Menthol. as ester . .· . .	3.4 to 4.8 p.c.	2.6 to 3.8 p.c.
Total menthol	46.3 to 54.2 p.c.	39.6 to 54.1 p.c.
Solubility in 70 p.c. alcohol	2.8 to 3.4 vol. and more, mostly showing opalescence when diluted.	2.8 to 3 vol. and more, in one instance only opalescence resulted upon dilution.

[1]) .Apotheker Ztg. 21 (1906), 927.
[2]) Report of Schimmel & Co. October 1911, 69.

HUNGARIAN PEPPERMINT OIL.

In the Experiment Station for the Cultivation of Medicinal Plants connected with the Royal Hungarian Agricultural Academy in Klausenburg-Kolozsvár a number of peppermint oils have been distilled concerning which K. Irk[1]) reports.

The Hungarian peppermint oil resembles the American more closely than any other. The plant contains 1.17 p.c. (computed with reference to dry material?) of oil with the following constants: $d_{15°}$ 0.9014 to 0.9192; α_D — 26,15 to — 32,40°; $n_{D20°}$ 1.4632 to 1.4769; menthol as ester 8 to 12.8 p.c.; total menthol 56.4 to 65.2 p.c.; menthone 7.4 to 13.2 p.c.; soluble in 2 to 5 vol. of 70 p.c. alcohol, in 1 to 2 vol. of 80 p.c. alcohol, and 0.5 vol. of 90 p.c. alcohol.

BOHEMIAN PEPPERMINT OIL.

An oil distilled in Bohemia had the following properties: $d_{15°}$ 0.905; α_D — 27° 22'; menthol as ester 8.7 p.c.; total menthol 59.9 p.c.[2]); soluble in 70 p.c. alcohol.

CHINESE PEPPERMINT OIL.

In China peppermint oil is produced, apparently in appreciable amounts, in the vicinity of Hongkong[3]). The parent plant is presumably *Mentha canadensis* var. *glabrata*, Gray[4]). There are but two reports of investigations[5]), probably of the same oil. $d_{15°}$ 0.918; α_D — 44° 2' and — 44° 40'; menthol as ester 12.6 and 13.5 p.c.; total menthol 64.0 and 64.2 p.c.; soluble in 2.5 vol. and more of 70 p.c. alcohol.

820. Oil of Mentha arvensis.

From the dry herb of *Mentha arvensis*, L., Ger. *Feldminze*, Schimmel & Co. obtained 0.22 p.c. of oil; $d_{15°}$ 0.857; α_D — 2° 44'.

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[1]) Kisérletügyi Közlemények 13 (1910), 3. f. böl. and 4. f. böl. Report from the chemical laboratory of Experiment Station for the Cultivation of Medicinal Plants of the Royal Hungarian Agricultural Academy in Kolozsvár; Report of Schimmel & Co. April 1911, 91; October 1911, 70.

[2]) Report of Schimmel & Co. April 1896, 47.

[3]) Daily Cons. and Trade Rep., Washington 17 (1914), No. 56, p. 906.

[4]) Perfum. Record 4 (1913), 33.

[5]) Report of Schimmel & Co. October 1910, 96. — Bull. Imp. Inst. 11 (1913), 434.

821. Oil of Mentha arvensis var. glabrata.

The oil of *Mentha arvensis* var. *glabrata,* Gray, growing in South Dakota, has been distilled by F. Rabak[1]) with a yield of 0.8 p.c. computed with reference to the fresh herb. The odor of the light yellow oil was similar to that of peppermint but caused to suspect the presence of pulegone. The taste was strongly peppermint-like and pungent. The oil which was soluble in one-half its volume of 90 p.c. alcohol, revealed the following constants: d 0.9267; $\alpha_D + 16° 27'$; A.V. 2.6; E.V. 13.1, corresponding to 4.6 p.c. of ester $C_{10}H_{16}OCOCH_3$; E.V. after acetylation 47, corresponding to 13.57 p.c. alcohol $C_{10}H_{19}OH$. Neither fuchsine solution nor Nessler's Reagent indicated the presence of aldehydes.

822. Oil of Mentha canadensis.

Wild mint, *Mentha canadensis,* L., Ger. *kanadische Minze,* which grows wild in North America, yields upon distillation an oil of reddish-yellow color and a strong odor reminding of pennyroyal. The yield from dry herb was 1.23 p.c.[2]). $d_{15°} 0.943$[2]); $d_{20°} 0.927$ to 0.935[3]); $\alpha_D + 16° 11'$ to $+ 20° 32'$. With twice its volume of 70 p.c. alcohol it yields a clear solution.

According to F. M. Gage[3]) the oil contains *pulegone,* the presence of which was established by means of Baeyer's bisnitroso compound. The melting point of this substance, not recorded by Baeyer, is at 81.5° according to Gage. In addition to pulegone the oil probably contains small amounts of *thymol* or *carvacrol.*

823. Oil of Mentha javanica.

Mentha javanica, Bl. (*Mentha lanceolata,* Benth.) is closely related to *Mentha canadensis,* L. and is also looked upon as a variety of *Mentha arvensis,* L. P. van der Wielen[4]) was the first to report on Javanese mint oil. It possessed an agreeable,

[1]) Midland Drugg. and Pharm. Review 43 (1909), 5.
[2]) Report of Schimmel & Co. October 1893, 45.
[3]) Pharm. Review 16 (1898), 412.
[4]) Pharm. Weekblad 41 (1904), 1081; Apotheker Ztg. 19 (1904), 930.

but not typical peppermint odor, a bitter taste and a light green color. $d_{15°}$ 0.9214; $[\alpha]_D + 4° 40'$; soluble in 1.5 vol. of 70 p.c. alcohol. Cooled to $-60°$ the oil congealed in part but liquified again at 15°. It contained much *pulegone* and little or no menthone or menthol.

An oil sent to the Botanical Institute in Buitenzorg[1]) by Dr. Carthaus of Java presumably was obtained from the same plant. $d_{20°}$ 0.974; $\alpha_{D20°}$ 12° 28' (direction not given); menthol as ester 5.2 p.c.; total menthol 44.9 p.c.

Presumably identical with this oil was the distillate sent by Carthaus to Schimmel & Co.[2]). It had a light green color and its odor did not even distantly remind of peppermint. It contained 55 p.c. of a compound, presumably *pulegone,* that reacted with neutral sodium sulphite. That portion of the oil which did not react with the sulphite had a decided linalool odor. $d_{15°}$ 0.9792; $\alpha_D + 11° 15'$; A.V. 0.7; E.V. 19.0; E.V. after acetylation 45.6; soluble in 1.8 vol. and more of 70 p.c. alcohol.

Very different in its properties was the Javanese mint oil examined by Roure-Bertrand Fils[3]). *Mentha arvensis* var. *javanica* is given as the parent plant. $d_{15°}$ 0.9979; $\alpha_D + 0° 24'$; A.V. 69.8(!); E.V. 49.7 = 13.8 p.c. computed as menthol as ester; E.V. after acetylation 153,3 -- 48,2 p.c. computed as total menthol; soluble in 1.5 vol. and more of 70 p.c. alcohol. On account of the high acid content all constants, with the exception of the density, were determined after the oil had been neutralized. Refrigeration of the dark yellow oil did not cause separation of menthol, even after inoculation with a few menthol crystals. Aldehydes and ketones were not present or only traces thereof, which shows that this oil bears no resemblance to the oils described above.

According to M. Greshoff[4]) the yield of oil from *Mentha arvensis* var. *javanica* observed in the Botanical Institute at Buitenzorg amounted to 1 p.c. $d_{30°}$ 0.943; α_D of the oil from the first cut $+ 10° 18'$, from plants of the second cut $+1° 24'$.

[1]) Jaarb. dep. Landb. in Ned.-Indië 1906, 45. Batavia 1907.
[2]) Report of Schimmel & Co. November 1908, 101.
[3]) Berichte von Roure-Bertrand Fils, April 1910, 65.
[4]) Report of Schimmel & Co. November 1908, 85.

824. Oil of Mentha aquatica. ·

From the dry herb of *Mentha aquatica,* L., Ger. *Wasser-minze,* Schimmel & Co.[1]) obtained 0.34 p.c. of a yellowish-green oil with a pennyroyal-like odor. $d_{15°}$ 0.880; a_D — 2° 14'.

An oil distilled at the request of Prof. Tschirch by the same firm from reliable, dry herb with a yield of 0.8 p.c. had very different properties[2]). Its color was pale yellow, the odor slightly minty. $d_{15°}$ 0.9553; a_D + 64° 56'; $n_{D20°}$ 1.48276.

Different again was an Hungarian oil from *Mentha aquatica* which showed the following constants according to K. Irk[3]): $d_{4°}^{15°}$ 0.9603; $a_{D20°}$ + 22.73°; $n_{D20°}$ 1.4900; soluble in 0.5 vol. of 90 p.c. alcohol. The color of the oil was a dark straw yellow and· its odor was pleasant, reminding of pennyroyal.

Poco-olie (Minjak poko or *Minjak poho)* is the name given in Java[4]) to the oil of *Mentha aquatica,* L. imported from China (Chinese *Loeng noo poho* or *Loeng nao poko*[5])). A genuine poco oil sent to the Botanical Institute at Buitenzorg had the following properties: $d_{20°}$ 0.909; $a_{D20°}$ — 42° 20'.

Synonymous with ·*Mentha aquatica,* L. is *Mentha citrata,* Ehrh., a plant that is popularly known in Florida as bergamot mint[6]). The oil obtained from the young, non-flowering plants (without roots) with a yield of 0.2 p.c. was light yellow in color and possessed an agreeable odor reminding of lavender and even more of bergamot: $d_{15°}$ 0.8826; a_D — 5° 35'; E.V. 31.28 = 10.95 p.c. of linalyl acetate; soluble in 2 vol. and more of 70 p.c. alcohol.

From the same plant but from frozen leaves an oil was obtained with like yield but with different properties: $d_{15°}$ 0.8895; a_D — 1° 41'; E.V. 111.28 = 38.95 p.c. ester (computed as linalyl acetate); soluble in 2 vol. and more of 70 p.c. alcohol.

[1]) Bericht von Schimmel & Co., October 1889, 55.

[2]) Report of Schimmel & Co. April 1913, 74.

[3]) Kiserletügyi Közlemenyek 14 (1911); Pharm. Zentralh. 52 (1911), 1113; Report of Schimmel & Co. April 1912, 132.

[4]) Report of Schimmel & Co. October 1908, 85. — Jaarb. dep. Landb. in Ned.-Indië, 1906, 45. Batavia 1907.

[5]) Bull. van het Koloniaal Museum te Haarlem No. 42, p. 179. Amsterdam 1909.

[6]) Report of Schimmel & Co. April 1904, 95.

Because of the higher ester content the odor of linaly acetate in this case was even more pronounced than in the foregoing oil. The causes of the very decided differences in the properties of the two oils have not been traced.

825. Oil of Spearmint.

Oleum Menthæ Crispæ[1]). — Krauseminzöl. — Essence de Menthe Crêpue.

Origin. In commerce American, English, German and Russian spearmint oils are differentiated. The botanical source of these oils differs. *"Krauseminze"* is a name applied to a number of mints with curly leaves and spearmint-like odor, the botanical relationship and nomenclature of which is exceedingly complicated, but which have been straightened out by A. Tschirch, J. ·Briquet and others[2]).

In North America (Michigan, Indiana, New York) and in England a large number of varieties of *Mentha spicata,* Huds. (*M. viridis,* L.) are cultivated as spearmint, thus in North America *M. spicata,* Huds. var. *tenuis* (Mchx.), Briq. and in England *M. spicata,* Huds. var. *trichoura,* Briq. In Germany (also in Korneuburg and Klausenburg) *M. spicata,* Huds. var. *crispata,* (Schrad.), Briq. is principally cultivated, less frequently *M. longifolia,* Huds. var. *undulata,* Briq. According to Tschirch, a Russian spearmint from the Government Poltava was a *M. verticillata,* L. var. *strabala,* Briq., another not curly form was *M. verticillata* var. *ovalifolia,* H. Br.

Production. Spearmint is distilled on a large scale in the United States, where it is also known as green mint, more particularly in Michigan and Indiana. The amount distilled has increased considerably in recent years. The former cultivation in Wayne Co., New York, has ceased almost entirely since 1911. In Michigan and Indiana the following areas were cultivated[3]): 800 acres in 1908; 1462 in 1910; 1726 in 1911; 2057 in· 1912; 3500 in 1913. Inasmuch as an acre yields[4]) about 20 lbs. of oil

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[1]) In the London Pharmacopœia for 1788, spearmint oil was designated *Oleum Menthæ Sativæ.* E. M. Holmes, Pharmaceutical Journ. 94 (1915), 29.

[2]) A. Tschirch, *Handbuch der Pharmakognosie,* vol. 2, p. 1100.

[3]) Reports of Schimmel & Co. 1908 to 1914.

[4]) Twentieth annual Report of the Bureau of Labor of the State of Michigan, p. 447.

the production of spearmint oil in 1913 must have amounted to about 70000 lbs. for those two states. The production in Germany is slight. This is also true of England where at present about 300 acres of spearmint are cultivated, not all of which, however, is distilled. As to the production in Austria-Hungary no data are available. So far as Russia is concerned, the oil production in the Ukraine[1]) amounts to 1000 lbs. and in the district of Epiphania of the Government Toula[2]) the production, according to a totally unbelievable statement, amounts to 200000 kg.

Cultivation. The method of cultivation is the same as that of peppermint. In Korneuburg[3]) the area of land not fertilized yielded 8.6 kg., the same area of fertilized land 15.87 kg. of dry herb. In Klausenburg[4]) three cuts were obtained, the third cut having no unfavorable influence on the wintering qualities of the plant.

Properties. Spearmint oil and German *Krauseminzöl* resemble each other so closely that the two are not differentiated in commerce. The oil is colorless or yellowish, or greenish-yellow, with the characteristic penetrating, persistent disagreeable odor of the spearmint. Age and exposure of the oil to air cause it to thicken and become darker.

AMERICAN AND GERMAN OIL. $d_{15°}$ 0.920 to 0.940; α_D — 34 to — 52°; $n_{D20°}$ 1.482 to 1.489; A. V. up to 2; E.V. 18 to 36; carvone content (sulphite method, see vol. I, p. 589) 42 to 60 p.c.; soluble in 1 to 1.5 vol. and more of 80 p.c. alcohol, the diluted solution becoming opalescent and even turbid. Somewhat different were the properties of the distillates obtained in the American branch of Schimmel & Co. in Garfield, N. J. The herb cultivated in the immediate vicinity of the factory was distilled fresh during the flowering period with a yield of 0.3 p.c. The oil had a specific gravity of 0.980, hence was appreciably heavier than the ordinary

[1]) Perfum. Record 5 (1914), 314.

[2]) Seifenfabrikant 34 (1914), 796.

[3]) E. Senft, Zeitschr. f. d. landwirtsch. Versuchsw. in Österreich 1914, fascicles 3/4.

[4]) B. Pater, Die Heilpflanzenversuchsanstalt der landwirtsch. Akademie in Kolozsvár, fascicle 1. Kolozsvár 1914.

commercial oils; $\alpha_D - 42° 30'$. The odor differed materially from that of the commercial oils; it was not at all peppermint-like but reminded distinctly of carvone. Cohobation of the aqueous distillate yielded relatively much oil that was heavier than water. In the production of the commercial oils, this part is possibly lost because of insufficient distillation which would account for the deviating specific gravity of those oils[1]). After the first cut toward the end of July, a second cut was made early in October. The yield, again computed with reference to the fresh material, amounted to only 0.18 p. c. The odor of the oil was not of so fine a quality and both density and angle of rotation were lower, namely 0.961 and $\alpha_D - 37° 20'$ respectively. Nevertheless the oil was heavier than the commercial oils, although no portions heavier than water were obtained this time[2]).

ENGLISH OIL. Two English oils examined by H. J. Henderson[3]) had the following constants: $d_{15°} 0.931$ and 0.927; $\alpha_D - -50°$ and $--50°$; soluble in 1 vol. of 90 p.c. alcohol, the addition of 6 to 7 vol. causing cloudiness turbidity.

AUSTRO-HUNGARIAN OIL[4]). Yield from non-dried material 0.52, from dried 1.8 to 2.5 p.c.; $d_{15°} 0.936$ to 0.952; $\alpha_D - 38$ to $-50°$; $n_{D20°} 1.489$ to 1.493; carvone content 61 to 72 p.c.; soluble in 1 vol. and more of 80 p.c. alcohol. The isolated carvone had the following properties: $d_{15°} 0.965$; $\alpha_D - 58° 7'$ to $-59° 50'$; soluble in 1 vol. and more of 80 p. c. alcohol.

RUSSIAN OIL. The Russian oil was distinguished by a high linalool and a low carvone content. Its odor was stale and only slightly spearmint-like, hence cannot be used in place of the other commercial oils. $d_{15°} 0.883$ to 0.889; $\alpha_D - -23$ to $-26°$; A. V. about 1; E. V. 15 to 25; carvone content (estimated!) 5 to 10 p.c.; linalool content about 50 to 60 p.c.; soluble in 2 to 3 vol. of 70 p.c. alcohol and in 1 vol. of 80 p.c. alcohol.

1) Report of Schimmel & Co. October 1896, 69.
2) Ibidem April 1897, 46.
3) Pharmaceutical Journ. 79 (1907), 506.
4) Comp. Report of Schimmel & Co. April 1909, 85 and K. Irk, Kiser-letügyi Közlemenyek 14 (1911); Pharm. Zentralh. 52 (1911), 1111; Report of Schimmel & Co. April 1912, 118.

Composition. R. Kane[1]) observed in the oil of *Mentha viridis* a crystalline constituent which possibly is identical with the fatty acid, m. p. 182 to 184°, observed (see below) by Nelson. J. H. Gladstone[2]) found *carvone* in the oil of green mint. With hydrogen sulphide he obtained a compound from which alkali separated an oil $C_{10}H_{14}O$, which deviated the ray of polarized light to the left as much as dill carvone does to the right. Gladstone designated this substance menthol, an unfitting name.

From German *Krauseminzöl*, F. A. Flückiger[3]) isolated a *l*-carvone with rather low rotation. A. Beyer[4]), however, found that the angle of rotation of the carvone from German oil is the same as that of caraway carvone and dill carvone. The amount of carvone in spearmint oil was found to be 56 p. c. by E. Kremers and O. Schreiner[5]). According to H. Trimble[6]) green mint oil contains a terpene boiling between 160 and 167.5°, according to Beyer a lævogyrate hydrocarbon that boils between 168 and 171°. J. W. Brühl[7]) infers the presence of *d*-pinene from the statements of Gladstone. According to F. B. Power[8]) the oil contains l-*limonene* and probably l-*pinene*.

While preparing *l*-carvone from a spearmint oil of unknown source, F. Elze[9]) obtained a by-product which possessed a more intense spearmint-like odor than the original oil. This waste oil had the following properties: $d_{15°}$ 0.917; $\alpha - 28°0'$. It contained 18 p. c. ester computed as acetate of dihydrocuminic alcohol. Distilled fractionally, the lowest portion was found to contain l-*phellandrene* (m. p. of nitrosite 105 to 105.5°). One fraction which had a decided spearmint odor was saponified. In the lye acetic and *valeric acids* were shown to be present. Of the alcoholic portion 15 p. c. consisted of *dihydrocuminic alcohol*

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[1]) Journ. f. prakt. Chem. 15 (1838), 163. — Liebig's Annalen 32 (1839), 286.

[2]) Journ. Chem. Soc. 25 (1872), 1 *et seq.*; Jahresber. d. Chem. 1872, 816.

[3]) Berl. Berichte 9 (1876), 473.

[4]) Arch. der Pharm. 221 (1883), 283.

[5]) Pharm. Review 14 (1896), 244.

[6]) Am. Jourh. Pharm. 57 (1885), 484.

[7]) Berl. Berichte 21 (1888), 156.

[8]) Descriptive Catalogue of Essential Oils. Published by Fritzsche Brothers. New York 1894, p. 33.

[9]) Chem. Ztg. 34 (1910), 1175.

(d_{15° 0.9539; $\alpha - 30\,^\circ 15'$; m. p. of naphthylurethane 146 to 147°), which, upon oxidation with Beckmann's mixture, yielded an aldehyde (m. p. of semicarbazone 198 to 199°) and an acid melting at 132". Upon saponification of the fraction the typical spearmint odor disappeared. Hence Elze regards the acetate of dihydro-cuminic alcohol as the characteristic odor bearer of the oil[1]).

E. K. Nelson[2]) has examined an authentic American spearmint oil which had been distilled in Michigan from selected material. $d_{25^\circ}^{25^\circ}$ 0.9290; α_{D25° — 52.16°; n_{D25° 1.4866; E. V. 12.4; E. V. after acetylation 36.4; soluble in an equal volume of 80 p. c. alcohol. It contained about 66 p. c. carvone. In the non-carvone-containing oil Nelson proved the presence of *phellandrene* (nitrosite) and l-*limonene* (nitrosochloride; m. p. of carvoxime 71 to 72°).

The American oil did not, however, contain the acetate of dihydrocuminic alcohol, which Elze regards as the bearer of the spearmint odor, but the *acetate of dihydrocarveol.* This alcohol Nelson isolated from fraction 100 to 150° (10 mm.) of the sapon-ified oil. With phthalic acid anhydride the alcohol reacted but imperfectly. Its isolation succeeded better by heating with suc-cinic acid anhydride to 125". The dihydrocarveol was identified by means of its constants, also by oxidation to dihydrocarvone (m. p. of semicarbazone 200 to 201" when quickly heated; m. p. of oxime 88 to 89°). The acetate of dihydrocarveol had a spear-mint-like odor.

In addition to *acetic acid* and probably *butyric, capronic* and *caprylic acids,* the oil contained 0.1 p. c. of a solid acid melting at 182 to 184° which Nelson also found in several other spear-mint oils.

According to H. Haensel[3]), German *Krauseminzöl* contains *dipentene* and *cineol.*

As found by Schimmel & Co.[4]), Russian oil consists for the most part, namely, 50 to 60 p. c., of l-*linalool.* Fraction 196 to

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[1]) H. Walbaum and O. Hüthig (Journ. f. prakt. Chem. 71 [1905], 472) have previously called attention to the strong spearmint-like odor of this ester. According to A. Blumann and O. Zeitschel (Berl. Berichte 47 [1914], 2623) carveol acetate also has a pronounced spearmint-like odor.

[2]) U. S. Dep. of Agriculture, Bureau of Chem., Circular No. 92.

[3]) Chem. Zentralbl. 1907, I. 1332.

[4]) Report of Schimmel & Co. April 1898, 46.

$200°$ had an optical rotation of $\alpha_D - 17°37'$ and upon oxidation yielded citral (m.p. of citrylnaphthocinchoninic acid $197°$). Fraction 170 to $175°$ ($\alpha_D - 24°54'$) which constituted about 20 p.c. of the oil yielded with iodol a crystalline addition product melting at $113°$, hence contained *cineol*. In addition it yielded a nitroso-chloride melting at $100°$, the formation of which is in all pro-bability attributable to l-*limonene*. The highest boiling fraction yielded the characteristic carvone hydrosulphide which melted at 210 to $211°$ ($[\alpha]_{D17°}$ in 5 p.c. chloroform solution $- 36°0'$). The amount of l-*carvone* in the Russian oil is estimated at 5 to 10 p.c.

826. Oil of Mentha silvestris.

At the request of Prof. Tschirch, of Bern, Schimmel & Co.[1]) distilled the dry herb of *Mentha silvestris,* L. and obtained a small amount of oil with a yield of 0.9 p.c. It was light yellow and had a stale, slightly minty odor. $d_{15°}$ 0.9852; $\alpha_D -132°52'$; $n_{D20°}$ 1.46856.

An oil distilled from *Mentha silvestris,* L. in Cyprus had been sent to Schimmel & Co.[2]) by the Imperial Institute in London. It had the following properties: $d_{15°}$ 0.9701; $\alpha_D + 31°30'$; $n_{D20°}$ 1.49544; A.V. 2.4; E.V. 20.9; E.V. after acetylation 171.4; soluble in 3 vol. of 70 p.c. alcohol, the dilute solution showing slight opalescence; the odor was slightly minty and the color yellow. The saponifi-cation number 171.4 after acetylation, which (computed as men-thol) would correspond to 54.8 p.c., can in no wise be regarded as a criterion, for the oil contains but little of *menthol*. The minty odor is due, in the first place, to *pulegone,* of which 40 p.c. are present (separated by means of neutral sulphite). In addition a *phenol,* presumably carvacrol, was shown to be present. Hence it may be assumed that this is esterified, hence increases the acetylation value. On account of the simultaneous presence of menthol, pulegone, and a phenol, the oil cannot be used in place of peppermint oil, pennyroyal oil, or origanum oil.

In connection with another Cyprus oil, also said to have been distilled from *Mentha silvestris,* the Imperial Institute[3])

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[1]) Report of Schimmel & Co. April 1913, 74.

[2]) *Ibidem* April 1910, 123.

[3]) Bull. Imp. Inst. 11 (1913), 432.

determined the following constants: $d_{15°}$ 0.9687; α_{D} + 31° 58'; S. V. 24.9; S. V. after acetylation 175.5; soluble in 2.5 vol. and more of 70 p.c. alcohol.

These two Cyprus oils appear to have been identical. Whether they were distilled from *Mentha silvestris*, however, remains doubtful in the light of a comparison of their constants with those of the oil distilled from material identified botanically.

827. Oil of Mentha rotundifolia.

A sample of Algerian oil of *Mentha rotundifolia*, L. that had been sent to Schimmel & Co.[1]) had a dark orange-yellow color and a musty, faint yet somewhat pungent odor that reminded but slightly of spearmint oil. $d_{15°}$ 0.9777; α_{D} – 37° 30'; $n_{D20°}$ 1.49471; A. V. 1.5; E. V. 71.2; E. V. after acetylation 209. The oil was miscible in all proportions with 90 p.c. alcohol and was soluble in 1 vol. of 80 p.c. alcohol; however, upon dilution the oil became decidedly turbid and oily drops separated.

828. Perilla Oil.

Origin and Properties. *Perilla nankinensis*, Decne. *(Perilla arguta*, Benth.; *Ocimum crispum*, Thunb., *Labiatæ)* is known in Japan as *Shiso* and its leaves are used as vegetable and spice. It contains a volatile oil, a sample of which had been sent to Schimmel & Co.[2]) from Yokohama. It was limpid, light to greenish in color, with a peculiar odor reminding of hay; yellow $d_{15°}$ 0.9265; α_{D} – 90°; $n_{D20°}$ 1.49835; soluble in 0.3 vol. and more of 90 p.c. alcohol, the diluted solution showing opalescence.

Composition. The oil reacted with both acid and neutral sulphite. By this means 50 p.c. of an *aldehyde* could be isolated, the odor of which bore some resemblance to that of cuminic aldehyde. Nevertheless, it was quite distinct, as had become apparent from the fact that it reacted with neutral sulphite. In connection with a sample that had been purified by means of the sulphite compound and had been distilled, first with steam and

[1]) Report of Schimmel & Co. April 1907, 107.
[2]) *Ibidem* October 1910, 146.

then in vacuum, the following constants were determined: b.p. 91° (4.5 mm.), 104° (9 mm.), 235· to 237° (750 mm.); $d_{20°}$ 0.9645; $d_{15°}$ 0.9685; α_D — 146°; $[\alpha]_D$ — 150.7°; $n_{D20°}$ 1.50693. The oxime, which likewise was lævogyrate, had a melting point of 102°, the phenylhydrazone melted at 107.5°. Both moist silver oxide and Beckmann's chromic acid solution oxidized it to the corresponding acid. This was almost insoluble in water and readily soluble in mostly all organic solvents. Recrystallized from dilute alcohol it resulted in white, shiny scales that melted at 130°.

This "perilla aldehyde" was later on investigated by F. W. Semmler and B. Zaar[1]) who recognized in it a *dihydrocuminic aldehyde* $C_{10}H_{14}O$ with the following constants: b.p. 104 to 105° (10 mm.); $d_{15°}$ 0.9617; $[\alpha]_D$ — 146°; n_D 1.50746; mol. refr. found 46.40, computed for $C_{10}H_{14}O/_2$ 45.52. The semicarbazone recrystallized from alcohol, melted at 199 to 200°.

By reduction with zinc dust in glacial acetic acid the corresponding perilla alcohol, $C_{10}H_{16}O$, was obtained: b. p. 119 to 121° (11 mm.); $d_{20°}$ 0.9640; $[\alpha]_D$ — 68.5°; n_D 1.49964. Its acetyl ester boiled at 123 to 126° (13 mm.); $d_{20°}$ 0.9785; $[\alpha]_D$ — 48°; n_D 1.48142. The chloride of perilla alcohol had the following properties: b. p. 99 to 101° (12 mm.); $d_{20°}$ 0.9861; $[\alpha]_D$ — 60°; n_D 1.49728. Reduced with sodium and alcohol, the chloride yielded limonene ($[\alpha]_D$ — 51.5°; m. p. of the tetrabromide 104 to 105°). Heated with acetic acid anhydride and sodium acetate, the perilla aldoxime yielded perillic acid nitrile (b.p. 116 to 118° under 11 mm. pressure; $d_{20°}$ 0.9439; $[\alpha]_D$ — 115°; n_D 1.49775). The corresponding perillic acid showed the following properties: m.p. 130 to 131° (recrystallized from dilute alcohol); b. p. 164 to 165° (10 mm.); $[\alpha]_D$ — 20°; (in 25 p.c. alcoholic solution), m.p. of dibromide 166 to 167°.

From the foregoing data it becomes apparent that the perilla aldehyde has the same configuration as limonene and that a reducible double linkage is in neighboring position to the aldehyde group. As a matter of fact, the reduction of perillic acid, in amyl alcoholic solution with sodium, yielded dihydroperillic acid, $C_{10}H_{16}O_2$; m.p. 107 to 109°; b.p. 152 to 153° (10.5 mm.); $[\alpha]_D$ + 0°; m.p. of dibromide 116 to 117°. The methyl ester boiled between

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[1]) Berl. Berichte 44 (1911), 52.

105 and 106° (11 mm.); $d_{19°}$ 0.9732; n_D 1.46768. Upon reduction of the ester with sodium and alcohol in the customary manner, Semmler obtained dihydroperilla alcohol, $C_{10}H_{18}O$; b.p. 114 to 115° (10 mm.); $d_{19°}$ 0.9284; $[\alpha]_D \pm 0°$; n_D 1.48191. The alcohol has a pleasant rose-like odor.

According to this investigation, perilla aldehyde is to be regarded as 1-methylal-4-*iso*propenyl hexene-1.
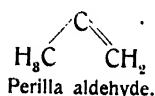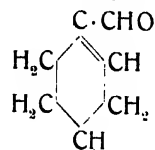
Perilla aldehyde.
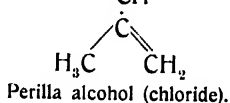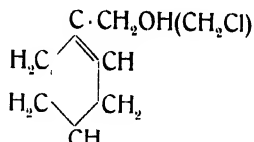
Perilla alcohol (chloride).
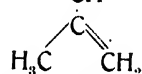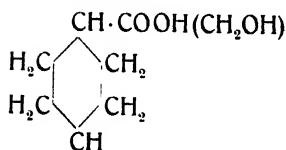
Dihydroacid. (Dihydroalcohol.)

Limonene.

829. Oil of Mosla japonica.

The herbaceous labiate *Mosla japonica,* Maxim., indigenous to Japan, yields, according to Shimoyama[1]), 2.13 p.c. of oil computed with reference to the dry herb. It is brownish-red, lævogyrate and has a specific gravity of 0.820 (?). It contains 44 p.c. of *thymol.* Fraction 170 to 180° probably contains cymene.

Y. Murayama[2]), who examined the oil more recently, obtained 2 p.c. of oil which contained, not thymol, but *carvacrol, also cymene.*

These two constituents, namely, carvacrol and *p*-cymene, were also found by Murayama and Nara[3]), who also found *α-pinene.*

1) Apotheker Ztg. 7 (1892), 439; Jahresb. f. Pharm. 1892, 465.

2) Journ. Pharm. Soc. of Japan 1909, November No.; Pharm. Zentralh. 51 (1910), 35.

3) Journ. Pharm. Soc. of Japan 1912; Chemist and Druggist 82 (1913), 19.

830. Oil of Elsholtzia cristata.

Y. Asahina and Y. Murayama[1]) have distilled and examined the oil of *Elsholtzia cristata,* Willd., a labiate which was formerly employed as an antipyretic and diuretic but which is now classed with the obsolete remedies. The dry herb yielded 2 p.c. of a yellowish volatile oil which became brown and which had a peculiar odor. $d_{15°}$ 0.970; α_D — 2.7°; A.V. 0; S.V. 1.8; S.V. after acetylation 14.7. It boiled for the most part between 210 and 215°. Neither shaking with alkali nor with bisulphite solution removed any appreciable portion of the oil. When heated with hydriodic acid methyl iodide was obtained. With semicarbazide hydrochloride a semicarbazone, m.p. 171°, was obtained; with hydroxylamine hydrochloride an oxime melting at 54°. The ketone recovered from these derivatives is a colorless, mobile oil, with a peculiarly aromatic odor, which boils at 87 to 88° (10 mm.), or 112° (31 mm.) or 210° (764 mm.); $d_{20°}$ 0.9817; $\alpha_D + 0°$; $n_{D20°}$ 1.48424. The authors name this ketone *Elsholtzia ketone.* It has the empirical composition $C_{10}H_{14}O_2$. Reduced with zinc amalgam and hydrochloric acid according to Clemmensen it afforded a poor yield of a compound $C_{10}H_{16}O$ which no longer gave a semicarbazone. Oxidation with potassium permanganate resulted in *iso*valeric acid which was characterized by the analysis of its silver salt and conversion into *iso*valeryl anilide (m.p. 115°). By the action of amyl nitrite and sodium on Elsholtzia ketone, Elsholtzia acid $C_6H_6O_3$, m.p. 134° resulted. Elsholtzia ketone appears to be a furane derivative, possibly of the formula

$$C_4H_2O \begin{matrix} CH_3 \\ CO \cdot CH_2 \cdot CH(CH_3)_2 \end{matrix}.$$
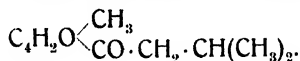
831. Patchouly Oil.

Oleum Foliorum Patchouli. — Patchoulïöl. — Essence de Patchouli.

Origin, A number of tropical labiates possess a characteristic, patchouly-like odor. All of these are used in the dried condition by the natives for perfuming carpets, shawls and other textiles, also for keeping insects out of clothes, but only a few are used for the production of the volatile oil.

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[1]) Arch. der Pharm. 252 (1914), 435.

105 and 106° (11 mm.); $d_{19°}$ 0.9732; n_{D} 1.46768. Upon reduction of the ester with sodium and alcohol in the customary manner, Semmler obtained dihydroperilla alcohol, $C_{10}H_{18}O$; b.p. 114 to 115° (10 mm.); $d_{19°}$ 0.9284; $[\alpha]_{D} \pm 0°$; n_{D} 1.48191. The alcohol has a pleasant rose-like odor.

According to this investigation, perilla aldehyde is to be regarded as 1-methylal-4-*iso*propenyl hexene-1.

C·CHO

H₂C⟨ ⟩CH

H₂C⟨ ⟩CH₂

CH

C

H₃C   CH₂

Perilla aldehyde.

C·CH₂OH(CH₂Cl)

H₂C⟨ ⟩CH

H₂C⟨ ⟩CH₂

CH

C

H₃C   CH₂

Perilla alcohol (chloride).

CH·COOH(CH₂OH)

H₂C⟨ ⟩CH₂

H₂C⟨ ⟩CH₂

CH

C

H₃C   CH₂

Dihydroacid. (Dihydroalcohol.)

C·CH₃

H₂C⟨ ⟩CH

H₂C⟨ ⟩CH₂

CH

C

H₃C   CH₂

Limonene.

829. Oil of Mosla japonica.

The herbaceous labiate *Mosla japonica,* Maxim., indigenous to Japan, yields, according to Shimoyama[1]), 2.13 p.c. of oil computed with reference to the dry herb. It is brownish-red, lævogyrate and has a specific gravity of 0.820 (?). It contains 44 p.c. of *thymol.* Fraction 170 to 180° probably contains cymene.

Y. Murayama[2]), who examined the oil more recently, obtained 2 p.c. of oil which contained, not thymol, but *carvacrol, also cymene.*

These two constituents, namely, carvacrol and *p*-cymene, were also found by Murayama and Nara[3]), who also found *α-pinene.*

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[1]) Apotheker Ztg. 7 (1892), 439; Jahresb. f. Pharm. 1892, 465.

[2]) Journ. Pharm. Soc. of Japan 1909, November No.; Pharm. Zentralh. 51 (1910), 35.

[3]) Journ. Pharm. Soc. of Japan 1912; Chemist and Druggist 82 (1913), 19.

6. *Microtæna robusta,* Hemsl. supplies the Chinese patchouly, which up to the present time has not entered European commerce. The plant is indigenous to Szetchuan, but also occurs in Kwangtung[1]).

From which plant the wild patchouly of New Guinea (sec p. 571)[2]) is obtained is not known.

Cultivation and distillation. Concerning the cultivation and distillation of patchouly in Singapore, J. Ficher, who formerly had a patchouly distillery, makes the following statements[3]):

The *Dhelum Wangi* of the natives (*Pogostemon Patchouli,* Pell.) is cultivated by the natives on suitable land along the coast. Inasmuch as the cultivated plant does not flower, it is reproduced by cuttings. Until these have produced roots they are protected against the sun by pieces of cocoanut shells. The harvest is conducted during dry weather. The green parts of the plant are cut, the dead leaves and stems are discarded, and the good leaves dried under shelter on bamboo trays so that the air can pass through from underneath. In order to effect the drying as rapidly as possible the leaves are turned frequently. When the leaves are almost dry and contain only enough moisture to admit of slight fermentation, they are piled and allowed to warm slightly. After that they are again spread out and allowed to dry completely. The addition of 25 p.c. of wild patchouly, *Dhelum Outan,* is said to improve the fragrance of the distillate.

The distillation is so conducted that the steam generated in a separate boiler is conducted into the still charged with leaves. The pressure of the steam should not exceed $1^{1}/_{3}$ atmospheres. If these conditions are maintained, the yield amounts to about 1.5 p.c. Steam under greater pressure is said to yield somewhat more, but also to diminish its quality. The stills are sometimes covered with a poor conducting coating so as to prevent condensation of the steam at the beginning of the operation[4]). —

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[1]) E. M. Holmes, Perfum. Record 4 (1913), 369 to 371, 418 to 420. — Comp. also Pharmaceutical Journ. 56 (1896), 222; 80 (1908), 349.

[2]) P. Preuß, Berichte d. deutsch. pharm. Ges. 19 (1909), 25.

[3]) Sawer, Odorographia. Vol. I, p. 297.

[4]) Additional information about the cultivation and distillation of patchouly in the Malaca peninsula is supplied by Wray, Curator of the Governmental Museum at Perak, in the Kew Bulletin for June, 1889. This is reprinted

From another distillery in Singapore it is reported[1]) that the distillation of a charge requires 36 hours and that the same material is distilled three times thus attaining a yield of 2.6 p.c. In Europe, where possibly the bulk of the patchouly oil used exclusively in perfumery, is produced, a yield of up to 4 p.c. is obtained because of the improved distilling apparatus used.

The output of a month's harvest in the Straits Settlements is estimated at 600 to 700 piculs ·· 35000 to 40000 kg. of patchouly herb[2]). Three harvests are gathered annually[3]).

It is noteworthy that the patchouly leaves contain acetone[1]), hence it must be contained in the aqueous distillate.

Investigation of the influence of the stage of development and of the fermentation of the leaves on the oily distillate. In order to place the arbitrary methods of harvest and distillation, as practiced in the tropics, on a more scientific basis, A. W. K. de Jong[5]), of Buitenzorg (Java), investigated the oil content of the patchouly plant in its various stages of growth for the purpose of ascertaining the best time for harvesting. With this end in view comparative water distillations were carried out with material representing different stages of growth: thus e. g. all first leaves from the tops were distilled together, also the second pairs of leaves, the third, the fourth, etc. Both weight and number of leaves were determined. Other parts of the plant were also investigated as to their oil content in order to ascertain whether their distillation was profitable or not. De Jong found that both so far as the genuine Singapore as well as the Java patchouly plants are concerned, the oil resides principally in the first three pairs of leaves, i. e. in the most

in the detailed chapter of Sawer's Odorographia, vol. I, p. 293 to 308. Comp. also Holmes, *loc. cit.* and P. Serre, Journ. d'Agriculture tropicale 5 (1905), 369; Report of Schimmel & Co. April 1906, 49. Furthermore: W. R. Tromp de Haas, Teysmannia 15 (1904), 474; Berichte über die pharmak. Lit. aller Länder 1905, 69.

[1]) Bull. de la chambre d'Agricult. de la Cochinchine 10 (1907), 37.
[2]) Berichte von Roure-Bertrand Fils October 1906, 37.
[3]) *Ibidem* April 1902, 38.
[4]) Verslag Plantentuin Buitenzorg 1894, 43.
[5]) Teysmannia 1906 and 1909. — Comp. also by the same author: *L'huile essentielle de patchouli,* Recueil trav. chim. des P.-B. 24 (1905), 309; Chem. Zentralbl. 1905, II. 1180.

recently developed ones. After that the oil content remains constant even though the leaves increase materially in weight. Hence it is recommended to cut the plants after five pairs of leaves have developed. Moreover, the leaves alone should be distilled since the handling of the stems is not profitable because of their slight oil content.

So far as fermentation is concerned, it was shown that a variation in the treatment of the leaves before distillation produces different results in the several varieties. Whereas the oils from fresh, dried and fermented materials varied but little so far as Singapore leaves are concerned, the difference in treatment of Java leaves had a decided influence on the character of the oil, as is revealed in the following table: —

No.	Condition of the leaves.	Color.	Odor.	$d_{15°}$	α_D	$n_{D20°}$	A.V.	E.V.	Solubility in 90 p.c. alcohol
				I. Singapore Oils.					
1.	fresh			0.9655	−51°18′	1.50820	1.5	2.0	sol. in 0.8 vol., the addition of from 1.5 to 5 vol. first causes turbidity, then the sol. becomes clear again.
2.	dry	light yellow	faint patchouly odor	0.9587	−50°58′	1.50766	—	1.1	sol. in 6 to 7 vol. a. m.
3.	fermented			0.9628	−52°23′	1.50784	0.9	1.5	sol. in 7 vol. a. m.
				II. Java Oils.					
4.	fresh		terpene-like	0.9344	−15°20′	1.50050	0.8	9.9	sol. in 0.3 vol. a. m. (sol. in abt. 10 vol. a. m. of 85 p.c. alcohol).
5.	fresh		faint patchouly odor	0.9450	-15°20′	1.50483	--	5.8	sol. in 0.6 vol. a. m. (not sol. in 10 vol. of 85 p.c. alcohol).
6.	dry	light yellow	calamus-like	0.9168	+ 3°15′	1.50030	—	6.1	sol. in abt. 10 vol. a. m.
7.	slightly fermented		calamus-like	0.9229	+ 2°32′	1.50058	0.8	4.9	sol. in abt. 10 vol. with separation of paraffin.
8.	strongly fermented		faint patchouly odor	0.9210	− 0°26′	1.50207	—	5.0	sol. in 8 vol. a. m.

With the exception of minor differences, the Singapore oils Nos. 1 to 3 agree very well among themselves and correspond with the Straits Settlements oils, with the exception that their odor is much weaker. From the more ready solubility of the oils distilled from fresh material it may possibly be concluded

that during the process of drying and fermenting difficultly soluble products are formed which pass over into the distillate. The other oils distilled from Java leaves not only differ greatly from the ordinary patchouly oils, but differ greatly among themselves according to the method by which the material had been prepared for distillation. The weak, but distinctly patchouly-like odor of the oil No. 5 obtained from fresh leaves (it is noteworthy that oil No. 4 had an odor that was but little pronounced) acquires a calamus-like odor when the leaves are but slightly fermented during the process of drying and becomes patchouly-like once more if the leaves are more strongly fermented. After the oils had stood for several months, these differences were no longer as pronounced as in the beginning. The optical rotation also is influenced by the drying and fermentation. At first it is changed to slightly dextrorotation, only to become slightly lævorotatory once more upon stronger fermentation.

Previous to distillation the stems were removed, since they contained but little oil. For purposes of drying the leaves were spread out in a shady place in layers 5 cm. in thickness. They were turned daily until they were completely wilted and brittle. For purposes of fermentation de Jong allowed the leaves to become half-dry and then piled them in heaps which were covered by a *tetampa*, a matting of bamboo which was weighted down with stones. The leaves were mixed thoroughly each day so as to insure an equal fermentation throughout. The process was continued until the temperature within the mass of leaves was no higher than the surrounding temperature. Varying according to the degrees of moisture in the leaves, the highest temperature ranged between 35 and 52°. A mouldy odor which almost always resulted was removed by spreading out the leaves for several days after the fermentation was over and before the distillation was begun.

The distillation was carried out with steam under 3 to 4 atmospheres pressure. In all cases after distillation the leaves were pressed, to remove water, dried and again distilled. The yield of oil from fresh leaves was much smaller than that from dried and fermented leaves. The following yields were obtained from the Java leaves: —

Condition of leaves.	Amount of fresh material worked up.	1. Distillation.	2. Distillation.	Total.
fresh	70 kg.	38 ccm.	114 ccm.	152 ccm.
fermented . .	70 „	375 „	30 „	405 „
dried	70 „	300 „	49 „	409 „
„	70 „	315 „	69 „ .	384 „
fermented .	70 „	350 „	28 „	378 „
„ . .	70 „	359 „	28 „ .	387 „

From the above data it becomes apparent that the distillation of fresh leaves is entirely irrational, for they yield but little oil. Most of the oil was obtained from the second distillation, *i. e.* after the leaves had been dried after the first distillation. Much larger yields are obtained, on the other hand, from dried and fermented leaves. The first distillation yields almost the entire oil and the second distillation yields relatively little oil. The total amount of oil is approximately the same whether the distillation be begun with dried or fermented leaves.

The situation is much the same with Singapore leaves. From 24 kg. of leaves in the fresh condition a first, single distillation yielded 20 cc. of oil, after drying, however, 77 cc., and after fermentation 86 cc. The fact that the total yield is lower is due to the circumstance that steam of but one atmosphere pressure was employed during the distillation.

The large difference in the yield obtained from fresh leaves on the one hand and from dried and fermented leaves on the other hand is attributed to the distribution of the oil cells[1] within the leaf, some being near the surface, others more remote therefrom. The fresh leaves give up the oil from the surface cells only. The wilting brought about by drying and fermentation causes the cell membrane to become more perishable so that the oil from the more deep-seated cells also can be separated by distillation. A subsequent formation of oil during the process of drying and fermentation does not take place, nor does the fermentation produce any oil, for the dried leaves yield as much oil as do the fermented ones.

[1] As to the location of the oil glands see H. Paschkis, Zeitschr. d. allg. österr. Apoth. Ver. 17 (1879), 415; Pharmaceutical Journ. III. 11 (1881), 813 and Fritz Mayer, *Systematisch-anatomische Untersuchung der Pogostemoneæ, Reichenb., unter besonderer Berücksichtigung der inneren Drüsen von Pogostemon und Dysophylla sowie der Patschuli-Droge. Inaug.-Dissert.* Erlangen 1909.

· In harmony with these views is the fact that the yield from fresh leaves is increased with the increase in pressure of the steam employed. De Jong assumes that with the increased steam pressure a larger number of cell walls are ruptured thus setting free more oil. These experiments also demonstrated that previous comminution of the fresh leaves greatly increased the yield of oil. Enzyme action does not come into consideration, for de Jong obtained the same results with leaves previously dipped into boiling water.

In this connection the petioles and the roots were examined as to their oil content. That of the former is very small, that of the latter somewhat larger. The root oil was heavier than water, hence has a different composition than that of the leaf oil.

Adulteration of Patchouli Leaves. Inasmuch as the leaves may be grossly adulterated, purchases should be made with care. Most common is an admixture of the leaves of *Ocimum Basilicum,* L. var. *pilosum* (family *Labiatæ*) known as *Ruku* by the Malays. The difference in their odor is entirely covered by contact with patchouly leaves. Frequently also the bales contain the leaves of *Urena lobata,* L. var. *sinuata* (family *Malvaceæ*), which grows as weed in the cocoanut plantations and which the Malays call *Perpulut.* Furthermore, the leaves of *Hyptis suaveolens* (see p. 573), *Plectranthus fruticosus,* Lam., *Lavatera Olbia,* L. and of *Pavonia Weldenii*[1]), are mentioned as adulterants.

In addition to these foreign leaves, which sometimes constitute 80 p.c. of the patchouly bales, as much as 50 p.c. of sand and soil and up to 35 p.c. of moisture have recently been observed.

Properties. In a general way three different types of patchouly oils may be differentiated. 1. Oils distilled in Europe from dry leaves. They constitute the bulk of the patchouly oil of commerce. 2. Oils distilled in Singapore. 3. Oils distilled from Java leaves including the dilem oils.

As already explained, patchouly oils are distilled from leaves obtained from different plants. A botanical determination of pressed material is therefore rather difficult. Hence the material

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[1]) See footnote on p. 568.

distilled may be mixed, so that the constants recorded herewith are not necessarily those of unmixed leaf varieties.

1. The oil distilled in Europe from dry Singapore leaves is a yellowish or greenish-brown, occasionally dark brown, very viscid liquid from which crystals sometimes separate upon standing. The odor of the oil is intense, persistent and penetrating. $d_{15°}$ 0.966 to 0.995; α_D —50 to --71°; $n_{D20°}$ 1.507 to 1.513; A.V. up to 5; E.V. 2 to 12. Mostly soluble in 0.5 to 1.5 vol. of 90 p.c. alcohol, the addition of more solvent occasionally causing temporary turbidity. Some oils dissolve only in 4 to 6 vol. of solvent[1]).

2. Imported Singapore oils. These are mostly of a lighter color and their odor is less intense than that of the preceding oils. $d_{15°}$ 0.960 to 0.980; α_D --47 to -- 61°; $n_{D20°}$ 1.508 to 1.512; A.V. up to 1; E.V. 1.5 to 7; some oils soluble in 0.5 to 1 vol. of 90 p.c. alcohol, mostly, however, in 5 to 8 vol. or even more difficultly soluble.

3. Java Patchouly oils. These oils which are also designated dilem oils, are characterized generally by a much fainter odor which is almost calamus-like, a lower lævorotation or rarely a slight dextrorotation, a lower specific gravity, and a lesser solubility. Whether the oils had been obtained from the flowering or non-flowering Java variety could not be ascertained. In the material distilled by Schimmel & Co. during the past ten years flowers were never found. $d_{15°}$ 0.925 to 0.935; α_D + 3° 15′ to --32° 17′[2]); A.V. 1 to 4; E.V. 6 to 18; soluble in 6 to 8 vol. and more of 90 p.c. alcohol. Other constants are recorded on p. 566.

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[1]) In connection with 1912 Penang leaves, M. Lehmann [Chem. Ztg. 37 (1913), 1589] observed deviations to the extent that the oils showed a lower specific gravity, a lower rotation and a poorer solubility than is otherwise the case. The density was as low as 0.95, the optical rotation as low as — 42°. Two of these oils which possessed an especially fine aroma, had even lower values: d 0.935 and 0.937; α_D —9 and —34°. Of 90 p.c. alcohol many of the oils required about 6 vol. to effect a clear solution. The yield, likewise, was poorer and in some instances amounted to but 2 p.c. An oil with a similar rotation (α_D —43° 31′) from Perak is described in Bull. Imp. Inst. 3 (1905), 230.

[2]) Comp. Verslag Plantentuin Buitenzorg 1893, 55. — Report of Schimmel & Co. November 1908, 95. — Berichte von Roure-Bertrand Fils April 1910, 64.

An oil distilled from Java leaves by Schimmel & Co. had the following properties: $d_{15°}$ 0.9665; α_{D} —53° 56'; $n_{\text{D}20°}$ 1.50939; A.V. 1.8; E.V. 2.0; soluble in 1 vol. of 90 p.c. alcohol.

Certain similarities with this oil were shown by an oil distilled from Sumatra dilem leaves. It had the following properties: $d_{15°}$ 0.9659; α_{D} —51° 16'; A.V. 5.1; E.V. 2.7; soluble in about 10 vol. of 90 p.c. alcohol. Judging from the constants of these two oils, the Singapore variety may be regarded as the botanical source.

An oil distilled in New Guinea from wild patchouly plants with a yield of 3.75 p.c., also a distillate from Mayotte[1]), were examined by Schimmel & Co.[2]) and found to possess normal properties.

Composition. Although the oil has been examined a number of times little is as yet known concerning the substances that are the bearers of the characteristic odor.

Patchouly alcohol, formerly known as patchouly camphor, occasionally separates from the oil after long standing, hence first attracted the attention of chemists. H. Gal[3]) proposed the formula $C_{15}H_{28}O$, but J. de Montgolfier[4]) found that its composition is more correctly expressed by the formula $C_{15}H_{26}O$. O. Wallach[5]) introduced the more rational designation patchouly alcohol.

Patchouly alcohol, $C_{15}H_{26}O$, crystallizes in transparent, water-white, hexagonal prisms topped with six-sided pyramids. It melts at 56° and is strongly lævogyrate: $[\alpha]_{\text{D}}$ in the fused condition —118°[4]), in chloroformic solution —97° 42'[5]). The elements of a molecule of water are so loosely combined that such dehydrating agents as hydrochloric acid, sulphuric acid and acetic acid anhydride remove them in the cold, and potassium bisulphate and zinc chloride upon heating. A hydrocarbon $C_{15}H_{24}$, named patchoulene results. Its odor is cedar-like. It boils at 254 to 256°; $d_{23°}$ 0.939[5]); $d_{15°}$ 0.9334; α_{D} —36° 52'[6]).

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[1]) Report of Schimmel & Co. April 1908, 121.

[2]) *Ibidem* April 1909, 76.

[3]) Compt. rend. 68 (1869), 406; Liebig's Annalen 150 (1869), 374.

[4]) Compt. rend. 84 (1877), 88.

[5]) Liebig's Annalen 279 (1894), 394.

[6]) Report of Schimmel & Co. April 1904, 71 to 75; April 1905, 61.

The compounds resulting by the replacement of halogen for the hydroxyl in patchouly alcohol are exceedingly unstable and split off hydrohalogen. The entire behavior of patchouly alcohol indicates that the hydroxy group is in tertiary position.

In an investigation of a larger amount of patchouly oil, Schimmel & Co.[1]) ascertained that 97 p.c. of the oil consists of substances that are valueless so far as its odor is concerned. About 40 to 45 p.c. boils between 260 and 280° and consists principally of several sesquiterpenes. The balance of the 97 p.c. is patchouly alcohol.

The following substances have been identified: traces of *benzaldehyde* (m. p. of semicarbazone 214°); *eugenol* (m. p. of benzoate 69 to 70°); *cinnamic aldehyde* (m. p. of semicarbazone 208°); in fraction 54 to 95° (4 mm.) an *alcohol* with a pleasant rose-like odor; also a *ketone* (m. p. of semicarbazone 134 to 135°) admixed with minimal amounts of one that resembled orris, as to odor; finally two *bases*. These basic substances were present in all of the low and sesquiterpene fractions and imparted to them a benumbing odor. A part of the bases extracted from the oil with the aid of dilute sulphuric acid boiled from 80 to 130°, another part between 135 and 140° (3 to 4 mm.). The lower boiling base formed a very hygroscopic hydrochloride melting indistinctly at 105 to 115° and a platinum salt melting at 208° which contained 35.9 p.c. C, 4.06 p.c. H, 26.94 p.c. Pt, and 5.36 p.c. N.

The base boiling between 135 to 140° (3 to 4 mm.) yielded a hydrochloride that melted sharply at 147.5° to 148.5° and the analysis of which corresponded with the formula $C_{14}H_{23}NO \cdot HCl$. In harmony with this formula is the Pt content of the platinum double salt melting at 175°, *viz.* 22.89 p.c.

In the oil examined by him, Wallach found large amounts of *cadinene* (m. p. of dihydrochloride 117 to 118°). Neither Schimmel & Co. nor H. von Soden and W. Rojahn[2]) were able to identify this hydrocarbon in the oils examined by them. This leads to the supposition that the oil examined by Wallach was obtained from another plant.

[1]) Report of Schimmel & Co. April 1904, 71 to 75; April 1905, 61.
[2]) Berl. Berichte 37 (1904), 3354.

By fractionation von Soden and Rojahn isolated from patchouly oil two sesquiterpenes: —

1. B. p. 264 to 265° (750 mm.), 95 to 96° (3 to 4 mm.); $d_{15°}$ 0.9335; $\alpha_{D20°}$ —58° 45'. It added bromine and hydrogen bromide. When dry hydrogen chloride was passed into its ethereal solution an oily hydrochloride was obtained which could not be made to solidify.

2. B. p. 273 to 274°; $d_{15°}$ 0.930; $\alpha_D + 0°$ 45'. In this case also a crystalline hydrochloride could not be obtained.

In the highest boiling portions J. H Gladstone[1]) observed a substance passing over with blue vapors, the so-called *azulene*[2]) or coerulein that has been noted in other oils.

832. Oil of Hyptis suaveolens.

Hyptis suaveolens (L.), Poit.[3]) which occurs from Mexico to southern Brazil, likewise in the Philippines and Java, China and the East Indies, is occasionally used in the dry condition as an adulterant of patchouly leaves.

From 200 kg. of this plant, which is known as, in the Tagal language, *sub-cabayog* in the Philippines, R. F. Bacon[4]) obtained only 27 g. (0.0135 p.c.) of a greenish oil which had a decided odor of *menthol*. Further investigation revealed this substance as the principal constituent of this oil. The small yield of oil, however, precludes its distillation on a larger scale.

To the natives of Java the plant is known as *daon rœrœkœ œtan*. Upon distillation in Buitenzorg, the fresh herb yielded 0.025 p.c. of an oil with the following properties: α_D — 16° 18'; A.V. 0.7; S.V. 14; S.V. after acetylation 31.7. Aldehydes were not present[5]).

An oil, probably from *Hyptis suaveolens* had previously been distilled in Buitenzorg. The fresh herb yielded about 1 p.c. α_D — 1° 56'; S.V. 17[6]).

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[1]) Journ. Chem. Soc. 17 (1864), 3; Jahresber. d. Chem. 1863, 545.

[2]) Comp. also de Jong, Recueil trav. chim. des P.-B. 24 (1905), 309; Chem. Zentralbl. 1905, II. 1180.

[3]) Illustrated in the Bericht von Roure-Bertrand Fils April 1902, 36.

[4]) Philippine Journ. of Sc. 4 (1909), A, 130.

[5]) Jaarb. dep. Landb. in Ned.-Indië, Batavia 1911, 47.

[6]) *Ibidem* 1906, 46.

833. Oil of Hyptis spicata.

The herb of *Hyptis spicata,* (Poit.) Briq., which grows abundantly in Florida, yielded upon distillation[1]) a very small amount (about 0.005 p.c.) of a light yellow oil with a faintly mint-like odor; $d_{15'}$ 0.915; $\alpha_D - 27°25'$; A.V. 2.17; E.V. 4.35; insoluble in 10 vol. of 80 p.c. alcohol.

The odor would seem to indicate the presence of small amounts of menthone and pulegone.

From the fresh leaves Th. Peckolt[2]) obtained 0.07 p.c. of oil.

834. Oil of Hyptis Salzmanni.

The fresh leaves of *Hyptis Salzmanni,* Benth. which frequently covers large areas in Brazil, yielded upon distillation 0.145 p.c. of an oil with an agreeable odor reminding of chamomile and balm[3]). $d_{23°}$ 0.9018.

835. Oil of Hyptis fasciculata.

The fragrant leaves of *Hyptis fasciculata,* Benth., which likewise occurs in Brazil, have been used as tea in dyspepsia, also for aromatic baths. The fresh leaves yield 0.15 p.c. of a volatile oil $d_{23°}$ 0.903. The odor resembled that of a mixture of balm and origanum oils[4]).

836. Oil of Peltodon radicans.

The fresh leaves of *Peltodon radicans,* Pohl. yielded, upon distillation, 0.08 p.c. of a light yellow, fragrant oil. $d_{23°}$ 0.890[5]).

837. Oil of Æolanthus suavis.

The fresh leaves of *Æolanthus suavis,* Mart., which is a native of tropical East Africa, when cultivated in Brazil, yielded, upon distillation 0.16 p.c. of a volatile oil with an agreeable patchouly-like odor. $d_{23°}$ 1.028[6]).

[1]) Report of Schimmel & Co. April 1904, 96.
[2]) Berichte d. deutsch. pharm. Ges. 14 (1904), 376.
[3]) Th. Peckolt, Berichte d. deutsch. pharm. Ges. 14 (1904), 377.
[4]) Th. Peckolt, *ibidem* 379.
[5]) Th. Peckolt, *ibidem* 375.
[6]) Th. Peckolt, *ibidem* 374.

838. Oil of Sweet Basil.

Oleum Basilici. — Basilicumöl. — Essence de Basilic.

Origin. In commerce two oils are distinguished, the ordinary oil of sweet basil and that from Réunion. In addition, oils have been obtained occasionally from not well defined varieties which, however, have not acquired any importance. Unfortunately the nomenclature of the several varieties of *Ocimum Basilicum*, L. is extremely complicated: different names have been applied to the same plant; one botanist regards as species what the other looks upon as variety or form; hence the botanical relation of the plants yielding sweet basil oil have not been cleared up satisfactorily. The oils, however, may be grouped in the following manner: —

1. The ordinary oil of commerce which is produced in Germany, France, Algiers and Spain. All of these oils have much the same properties and constituents (methyl chavicol and linalool). An oil produced in central Africa[1]) likewise resembled those already named. *Ocimum Basilicum*, L. is regarded as the original species from which these oils are obtained. In southern France the following varieties are cultivated and used in the production of the oil[2]): *Ocimum Basilicum* var. *purpurascens,* Benth. (*O. nigrum,* Thouin), the violet-red variety, *O. B.* var. *thyrsiflorum,* Benth., the common white variety, *O. B.* var. *album,* Benth., the lactuca-leaved variety and *O. B.* var. *crispum,* E. G. Camus, the curly-leaved variety. The last variety is said to be best suited to the production of oil, both as to yield and to fragrance of product. The yields of the French varieties are recorded in the table on page 576. In Germany the fresh herb yielded 0.02 to 0.07 p.c. of oil.

2. Réunion Oil. The parent plant is unknown. The oil differs from that reported under No. 1 by its camphor content. The Comora islands Mayotte and Joanna (Anjouan) have supplied oils with like properties[3]).

3. Javanese oil from *Ocimum Basilicum*, L., var. *selasih hidjau,* like the following, has been distilled occasionally in Buiten-

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[1]) Report of Schimmel & Co. April 1914, 22.

[2]) *Botanische Untersuchung der angebauten Basilicumarten von* E. G. Camus *und* A. Camus. Berichte von Roure-Bertrand Fils October 1910, 23.

[3]) Report of Schimmel & Co. October 1909, 26; October 1913, 27. — Berichte von Roure-Bertrand Fils October 1912, 76.

zorg. The fresh herb yielded 0.2 p.c. It differs from the ordinary oil by its dextrorotation and its content of the olefinic terpene, ocimene. For further detail see Composition.

4. Javanese oil from *Ocimum Basilicum*, L., var. *selasih mekah* or *selasih besar*, yield 0.18 to 0.32 p.c. It contains eugenol as does the oil of the small basil, *Ocimum minimum*, L.

5. The oil from an unknown Basilicum species of Mayotte [1]) likewise contained eugenol.

Properties. *German and French Oil.* As already stated, the German and French oils have the same properties as have the commercial oils from Spain and Algiers. They are yellow liquids of an aromatic, penetrating, esdragon-like odor. $d_{15°}$ 0.904 to 0.930; a_D —6 to —22°; $n_{D20°}$ 1.481 to 1.495; A.V. up to 3.5; E.V. 1 to 12; soluble in 1 to 2 vol. and more of 80 p.c. alcohol, the solution at times opalescent or separating paraffin. As to the properties of the oil from the French varieties enumerated on p. 575 the following table from the reports of Roure-Bertrand Fils for October 1910, 39, affords detailed information [2]): —

Constants	*Ocimum Basilicum*, L.					
	var. *thyrsiflorum*		var. *crispum*	var. *album*	var. *purpurascens*	
	Harvest 1910	1909	1910	1910	1910	1909
$d_{15°}$	0.9168	0.9125	0.9123	0.8975	0.8959	0.9100
a_D	—10°52'	—11°28'	—10°30'	—12°54'	—13°52'	—10°14'
a_D of the acetyl-ated oil	+1°36'	+1°34'	+0°30'	+0°2'	+1°52'	+3°28'
$n_{D20°}$	1.488	1.484	1.484	1.479	1.477	1.477
A. V.	2.8	1.4	2.1	0.7	3.5	2.1
E. V.	5.6	3.5	4.9	7.0	9.8	7.7
Ester content, comp. w. ref. to linalyl acetate	1.96 p.c.	1.22 p.c.	2.45 p.c.	1.71 p.c.	3.43 p.c.	2.68 p.c.
E. V. after actl. .	116.9	114.8	116.9	130.2	126.7	117.6
Alcohol content, comp. w. ref. to linalool	35.19 p.c.	34.50 p.c.	35.19 p.c.	39.66 p.c.	38.46 p.c.	35.43 p.c.
Yield	0.0855 p.c.	—	0.1285 p.c.	0.0780 p.c.	0.0370 p.c.	—

The methylchavicol content of all samples, ascertained by means of their methoxyl values, amounted to about 55 p.c.

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[1]) Report of Schimmel & Co. April 1908, 120.
[2]) Comp. also G. Laloue, Bull. Soc. chim. IV. 11 (1912), 491.

Réunion Oil (including the Comora oils mentioned above). This oil differs from the preceding ones by its camphor-like odor. d_{15° 0.945 to 0.987; $\alpha_D + 0°22'$ to $+ 12°$; n_{D20° 1.51505 to 1.51753; A. V. up to 3; E. V. 9 to 22; soluble in 3 to 7 vol. of 80 p.c. alcohol, occasionally even in 2 to 3 vol.; in individual cases with the separation of paraffin.

Composition. In 1831 Bonastre[1]) found a solid constituent in basilicum oil, the so-called basilicum camphor. An analysis made by J. Dumas and E. Péligot[2]) corresponded with the formula $C_{10}H_{22}O_3$, hence with terpin hydrate. Presumably this substance had been formed by the addition of water to either pinene or linalool. The French oil has been examined by J. Dupont and Guerlain[3]). They found *methyl chavicol* and *linalool* as principal constituents.

Similar in composition was the oil examined by J. Bertram and H. Walbaum[4]). The lowest boiling fractions contained *cineol*[5]) (m. p. of cineol iodol 112°). The fraction boiling in the neighborhood of 215° contained methyl chavicol (m. p. of homoanisic acid 85°). The methyl chavicol content, computed from the methoxyl value amounted to 24 p.c. The fraction boiling about 200° was alcoholic in its nature. There can scarcely be any doubt but that this fraction, as is the case with the French oil, consists of linalool. Camphor is not contained in either the German or the French oil.

In the oil from Réunion Bertram and Walbaum found the following substances: 1. d-*α-Pinene* (m.p. of pinene nitrolbenzylamine 123°). 2. *Cineol* (cineol hydrogen bromide; m.p. of cineol-iodol 112°). 3. d-*Camphor* (m.p. of camphor oxime 118°). 4. *Methyl chavicol*. The bulk of the oil consists of this substance. Its identity with *p*-allylphenol methyl ether was established by its oxidation to homoanisic and anisic acids, also by converting it into the isomeric anethol. The quantitative methoxyl determi-

[1]) Journ. de Pharm. II, 17 (1831), 647; Pharm. Zentralbl. 1831, 848.

[2]) Liebig's Annalen 14 (1835), 75.

[3]) Compt. rend. 124 (1897), 300. — Bull. Soc. chim. III. 19 (1896), 151.

[4]) Arch. der Pharm. 235 (1897), 176.

[5]) The presence of cineol in basilicum oil had previously been rendered probable by E. Hirschsohn (Pharm. Zeitschr. f. Russl. 32 [1893], 419) when he obtained crystals upon the addition of iodol.

nation according to Zeisel's method revealed a content of 67.8 p.c.
Linalool is not contained in this oil.

From a small sample of Réunion oil Dupont and Guerlain
isolated a crystalline substance melting at 64 to 65°. The amount
was too small for investigation.

The oil from the *selasih hidjau* variety from Java ($d_{25°}$ 0.948 and
$d_{10°}$ 0.962; $\alpha_D + 0.35°$ and $+0°50'$) has been examined by P. van Rom-
burgh[1]). He found cineol (iodol reaction), methyl chavicol and low-
boiling hydrocarbons, presumably pinene and an olefinic terpene.

The same investigator[1]) examined the oil from the variety
selasih besar or *mekah* ($d_{20°}$ 0.890 to 0.940; $\alpha_D - 11.25$ to $- 18°$).
He identified the olefinic terpene *ocimene* (see vol. I, p. 280) and
30 to 46 p.c. *eugenol*. Of the same botanical origin was possibly
an oil sent to Schimmel & Co.[2]) from the island Mayotte which
had a high eugenol content (m. p. of benzoyl compound 70°).
It had the following properties: $d_{15°}$ 0.9607; $\alpha_D - 14°54'$; A.V. 4.7;
E.V. 3.7; E.V. after acetylation 140.1; soluble, with slight turbidity,
in 7 vol. and more of 90 p.c. alcohol.

839. Oil of Ocimum canum.

Roure-Bertrand Fils[3]) have examined an oil of *Ocimum
canum*, Sims (*O. americanum*, L.) that had been sent to them
from Dabakala on the Ivory Coast. The plant was then distilled
by this firm in France, yielding the same oil, with a yield of
0.65 p.c., as the one obtained from Africa. The botanical deter-
mination was carried out by E. G. Camus.

Soon after its preparation the oil deposited needle-shaped
crystals, several centimeters in length, at ordinary temperature.
Upon warming the oil gently with the hand, it formed a strongly
refractive, slightly yellow liquid with the following properties:
$d_{32°}$ 1.0330; $\alpha_{D30°} - 2°30'$; A.V. 0; E.V. 301,4; soluble in $2^1/4$ vol.
and more of 75 p.c. alcohol and in all proportions of 80 p.c.
alcohol. The solid substance melted at 35 to 37° and proved to
be identical with *cinnamic acid methyl ester*. The acid, separated
from the saponification liquid, melted at 133°, the melting point

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[1]) Verslag Plantentuin Buitenzorg 1898, 28; 1901, 58. — Koninklijke
Akademie van Wetenschappen te Amsterdam 1900, 446; 1904, 700; 1909, 15.

[2]) Report of Schimmel & Co. April 1908, 120.

[3]) Berichte von Roure-Bertrand Fils October 1913, 19.

of cinnamic acid. The saponification value corresponds to about 87 p.c. of methyl cinnamate. The non-saponifiable portions of the oil appear to consist of strongly lævogyrate hydrocarbons.

Some time ago Schimmel & Co.[1]) likewise examined an oil of *Ocimum Canum* that had been sent to them from Central Africa. It had the following constants: d_{30° 1.0431; α_D $-2°25'$; n_{D30° 1.55611; A.V. 0.6; E.V. 289.8; not completely soluble in 10 vol. of 70 p.c. alcohol, but soluble in 1 vol. and more of 80 p.c. alcohol. Gently heated, the oil constituted a yellow liquid, which, however, congealed largely at room temperature. The crystals, removed by suction, after recrystallization had the melting point of methyl cinnamate (36°). Upon saponification of the ester, cinnamic acid (m.p. 133°) and methyl alcohol could be isolated. The latter was characterized by its boiling point and oxidation to formic acid.

The liquid which was obtained by filtering the crystals from the thoroughly chilled oil, still had a decided odor of methyl cinnamate and showed the following constants: d_{15° 1.0404; n_{D20° 1.54932. By means of repeated distillation under ordinary pressure, when it passed over between 230 and 260°, it was freed as much as possible of methyl cinnamate (b.p. 255 to 260°), but not completely. Saponification of the lower fraction left only a small amount of oil of a faintly camphor-like odor. However, it was impossible to identify camphor by means of semicarbazide or borneol by means of phenyl*iso*cyanate.

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Several years ago E. Charabot[2]) described an oil that was said to have been obtained from *Ocimum canum*, Sims. It contained relatively much d-*camphor*. Judging by the above investigations it must be assumed that Charabot had an oil from a different species of *Ocimum*.

An oil from the island of Mayotte described by Schimmel & Co.[3]) as having been obtained from *Ocimum canum*, also contained relatively much d-*camphor* and in this respect corresponds to the oil of Charabot.

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[1]) Report of Schimmel & Co. April 1914, 72.
[2]) Bull. du Jardin colonial 1903; Berichte von Roure-Bertrand Fils April 1908, 33.
[3]) Report of Schimmel & Co. April 1908, 120.

840. Oil of Ocimum minimum.

From southern France Schimmel & Co.[1]) obtained two distillates from *Ocimum minimum* known as *Basilic nain* or *petit basilic.* In their constants they corresponded with the commercial German and French basilicum oils from *Ocimum Basilicum,* L. or *grand basilic,* but their peculiar, spicy odor was very different as was also their chemical composition. They contained about 14 p.c. *eugenol* which was characterized by its benzoyl compound melting at 69°. In addition linalool seemed to be present. At least the phenol-free oils had a decided odor of linalool. Whether they also contained methyl chavicol, which predominates in the commercial oils, could not be ascertained because of the smallness of the samples. On this account little more could be accomplished than to determine the general constants.

N°.	$d_{15.0}$	α_D	A.V.	E.V.	Phenol content	Solubility in	
						80 p.c. alcohol	70 p.c. alcohol
1.	0.9102	$-11°58'$	5.3	12.5	14 p.c.	in 0.6 vol. a. m.	in 2 vol., with 10 vol opalescence
2.	0.8901	$13°36'$				in 1 vol. a. m.	in 2.5 vol., 4.5 vol. and more cause turbidity

841. Oil of Ocimum gratissimum.

An oil of *Ocimum gratissimum,* L. examined by Roure-Bertrand Fils[2]) had been distilled in Debakala on the Ivory Coast. Its odor was that of ajowan oil. It had the following constants: d_{15} 0.9105; α_D $+0°58'$; soluble in 1.2 vol. of 80 p.c. alcohol. It contained 44 p.c. of phenol which was identified as *thymol* by its melting point, namely 49.5 to 50.5°.

The material had been examined botanically by E. G. Camus.

A like oil was obtained by Schimmel & Co.[3]) from Central Africa. It had the following properties: d_{15} 0.9055; α_D $+0°50'$; n_{D20} 1.49373; A.V. 0.4; E.V. 3.5; not completely soluble in 10 vol. of 70 p.c. alcohol, soluble in 7 vol. and more of 80 p.c. alcohol with very slight opalescence, and in 0.5 vol. and more of 90 p.c. alcohol. The oil was light brown in color, had a thyme-like odor, and contained 35 p.c. *thymol.*

[1]) Report of Schimmel & Co. April 1909, 20.

[2]) Berichte von Roure-Bertrand Fils October 1913, 21.

[3]) Report of Schimmel & Co. April 1914, 72.

842. Oil of Ocimum viride.

Ocimum viride, Willd., the mosquito plant, is rich in a spicy volatile oil contained in oil cells of the leaves for which reason it is recommended against mosquitoes. Four plants placed around a bed are said to afford better protection than a mosquito net. However, this effectiveness is questioned by J. P. Quinton [1]).

The leaves sent from Sierra Leone in March 1907 to the Imperial Institute in London were distilled by E. Goulding and R. G. Pelly [2]) who obtained a yield of 0.35 p.c. of an orange-yellow oil of an aromatic thyme-like odor and a spicy, burning taste: $d_{15°}$ 0.9115; $[\alpha]_D$ +1° 30′; soluble in all proportions of 90 p.c. alcohol. Distilled under ordinary pressure the following fractions were obtained: 25 p.c. between 165 and 180° ($d_{15°}$ 0.8614; $[\alpha]_D$ +0° 33′); 20 p.c. between 180 and 200° ($d_{15°}$ 0.8804; $[\alpha]_D$ +1° 40′); 20 p.c. between 200 and 220° ($d_{15°}$ 0,9164; $[\alpha]_D$ +2° 38′); 20 p.c. between 220 and 235° ($d_{15°}$ 0.9548; $[\alpha]_D$ +3° 38′); and 10 p.c. between 235 and 250° ($d_{15°}$ 0.9565; $[\alpha]_D$ +5° 14′).

Of its constituents the following were identified: *thymol* (32 p.c.), *alcohols* (14 p.c., computed as $C_{10}H_{18}O$), esters (2 p.c., computed as $C_{10}H_{17}OCOCH_3$). The balance consisted of a terpene or a mixture of terpenes with high refractive power, lemon-like odor, having the following constants: b.p. 160 to 166°; $d_{15°}$ 0.8456; α_D +0° 10′.

According to an investigation in the Imperial Institute, leaves obtained in September 1904 from northern Nigeria yielded 1.2 p.c. of volatile oil. The difference in the yield is explained by pointing out that the leaves were collected in a different season.

Schimmel & Co. [3]) examined an oil sent to them by the Imperial Institute. It had a thyme-like odor, was of a brown color and showed the following constants: $d_{15°}$ 0.9338; α_D +0°; $n_{D20°}$ 1.50418. The oil was soluble in 4 vol. and more of 70 p.c. alcohol, the diluted solution being opalescent. An assay with 5 p.c. caustic alkali revealed a 52 p.c. phenol content identical with *thymol*.

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[1]) Annual Report on Government Gardens and Parks in Mysore for the year 1902/03, 11. This report contains a good illustration of *Ocimum viride,* Willd. and of the several parts of the plant.

[2]) Proceed. Chem. Soc. 24 (1908), 63.—Bull. Imp. Inst. 6 (1908), 209.

[3]) Report of Schimmel & Co. October 1911, 62.

843. Oil of Ocimum sanctum.

In the Philippines *Ocimum sanctum*, L. is frequently cultivated in the gardens. From the leaves, distilled 48 hours after they had been picked, R. F. Bacon[1]) obtained 0.6 p.c. of a green oil with a sweetish, anise-like odor. It had the following constants: $d_{30°}^{80°}$ 0.952; $\alpha_D + 0°$; $n_{D30°}$ 1.5070; S.V. 2.8. Fraction 85 to 95° (9 mm.) contained considerable amounts of *methyl chavicol*, which was characterized by oxidation to homoanisic acid melting at 85°.

Later B. T. Brooks[2]) identified *cineol* (hydrogen bromide addition product) and *linalool*.

844. Oil of Ocimum pilosum.

The oil of *Ocimum pilosum*, Roxb.[3]) has been prepared by Kshitibhusan Bhaduri[4]). It is contained in the fresh seeds, also in the leaves, but not in the dried seeds. This peculiarity the author explains by stating that the very volatile oil volatilizes or resinifies during the process of drying. The oil is a pale yellow, very mobile liquid that has an odor of lemongrass oil: $d_{25.5°}$ 0.8872; $\alpha_D -3.7°$; $n_{D24.5°}$ 1.4843. It contains 34 p.c. of *citral* and 41 p.c. of *citronellal* (characterized by its condensation products with pyrouvic acid and β-naphthylamine), *cineol, limonene* and *thymol*. When shaken with an aqueous solution of sodium sulphite and sodium bicarbonate 75 p.c. of the oil was absorbed.

845. Oil of Ocimum micranthum.

From the fragrant leaves of *Ocimum micranthum*, Willd., known as "large marjoram" in Brazil, Th. Peckolt[5]) obtained 0.14 p.c. of volatile oil; $d_{23°}$ 0.982.

The fleshy, pleasantly aromatic leaves of *O. carnosum*, Lk. et Otto, yield, according to the same investigator[6]), 0.25 p.c. of volatile oil.

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[1]) Philippine Journ. of Sc. 5 (1910), A, 261.

[2]) *Ibidem* 6 (1911), A, 345.

[3]) According to *Index Kewensis Ocimum pilosum*, Willd. is synonymous with *O. Basilicum*, L.; *O. pilosum*, Roxb. is not mentioned in the *Index*.

[4]) Journ. Americ. Chem. Soc. 36 (1914), 1772.

[5]) Berichte d. deutsch. pharm. Ges. 14 (1904), 374.

[6]) *Ibidem* 373.

Family: SOLANACEÆ.

846. Oil of Datura Stramonium.

Upon the distillation with water vapor of the (dried?) leaves of *Datura Stramonium*, L., H. Haensel[1]) obtained 0.045 p.c. of a dark brown oil with a tobacco-like odor that solidified at 20°; $d_{30°}$ 0.9440. After the oil, in ethereal solution, had been decolorized with animal charcoal and after removal of the solvent the A. V. was 52.4, the S. V. 9.57.

847. Oil of Fabiana imbricata.

From the ethereal extract of the leaves of *Fabiana imbricata,* Ruiz et Pavon, H. Kunz-Krause[2]) obtained, upon steam distillation and shaking of the aqueous distillate with ether, a small amount of volatile oil. A small amount of this distilled over at 130°, but the bulk of the oil passed over at 275°. The principal constituent, designated *fabianol,* yielded, upon analysis, results corresponding with the formula $C_{54}H_{90}O_4$.

848. Tobacco Oil.

For the production of tobacco several species of the solanaceous genus *Nicotiana* are cultivated. The fermented tobacco contains a volatile oil that can be obtained by distillation with steam. At the request of H. Thoms[3]), Schimmel & Co. distilled 15 kg. of well fermented tobacco from the Uckermark, yielding 6 g. of oil that was examined by Thoms. The oil was dark in color, thick like a balsam and possessed an odor reminding of chamomile. When the ethereal solution was shaken with dilute potassa solution the latter took up small amounts of phenol. Upon distillation under ordinary pressure the bulk of oil came over between 295 and 315° as a green colored distillate.

A very different volatile oil results when the tobacco is smoked. In a special apparatus[3]) Thoms obtained from 20 kg.

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[1]) Chem. Zentralbl. 1910, II. 1539.

[2]) Arch. der Pharm. 237 (1899), 10.

[3]) Paper read at the *71. Versammlung der Gesellschaft deutscher Naturforscher und Ärzte in München 1899.* Chem. Ztg. 23 (1899), 852.

of smoked tobacco 75 g. of an ethereal oil which contained a *phenol* and probably *furfurol*. Deprived of its phenol, the oil began to distill at 190°; the larger portion went over between 220 and 230°, another portion between 230 and 260°. The presence of sulphur and nitrogen was ascertained. The oil must contain a strongly poisonous substance, for, while working with it, it produced headache, a tendency to vomit, dizziness and trembling of the legs.

S. Fraenkel and A. Wogrinz[1]) were of the opinion that the bearer of the tobacco aroma is a volatile alkaloid not identical with nicotine.

More recently W. Halle and E. Pribram[2]) succeeded in extracting from 300 kg. of Hungarian tobacco of medium quality (*Nicotiana rustica*, L.?) with an organic solvent and the aid of heat, 140 g. (= 0.047 p.c.) of a yellow oil which had a benumbing effect and possessed a strong odor of tobacco. It was absolutely free of nitrogen, reacted acid toward litmus and boiled between 77 and 100° under 20 mm. pressure. Although it had previously been shaken with soda solution, it again showed an acid reaction after distillation. The acid was identified as iso*valeric acid* by its odor, boiling point determination, density, titration and analysis of its barium salt. Fraction 72 to 82° (18 mm.) contained a hydrocarbon to which possibly the formula $C_{10}H_{18}$ or $C_{11}H_{20}$ may be assigned. As "Abbau" product the hydrocarbon yielded an acid insoluble in chloroform which appears to be identical with terephthalic acid and an acid solution in chloroform which presumably is *iso*butylacetic acid. Tobacco oil also contains a high-boiling oxygenated substance.

Family: SCROPHULARIACEÆ.

849. Leptandra Oil.

Leptandra is defined by the U. S. P. as the dried rhizome and rootlets of *Veronica virginica*, L. (*Leptandra virginica*, Nuttall). 55.56 kg. of this drug were extracted by F. B. Power

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[1]) Monatsh. f. Chem. 23 (1902), 236; Chem. Zentralbl. 1902, I. 1370.
[2]) Berl. Berichte 47 (1914), 1394.

and H. Rogerson[1]) with hot alcohol, whereby they obtained
19.79 kg. of extract. Two kg. of this extract were distilled with
steam, yielding 0.9 g. of oil corresponding to 0.016 p.c. of the
drug. Under a pressure of 25 mm. the oil distilled between
120 and 160°. It was a dark brown, mobile liquid of a strong
penetrating odor. With ferric chloride it gave no color reaction.

850. Oil of Buddleia perfoliata.

The woody shrub *Buddleia perfoliata,* H. B. et K., is a native
of the temperate areas of the province Mexico and is known as
Salvia bolita. In Xochimilco the leaves and flowers were distilled
and the resulting oil sent to Schimmel & Co.[2]) by the Instituto
Medico Nacional of Mexico. The oil is light yellow in color
and has a peculiar but agreeable odor which is possibly due
to fatty aldehydes small amounts of which are present in the
oil, but which could not be identified because of the small
amount of material. $d_{15°}$ 0.8862; $\alpha_D + 25°$; A. V. 0.6; E. V. 8.1;
soluble, with slight turbidity, in 4 to 5 vol. of 90 p.c. alcohol.

851. Limnophila Oil.

According to B. T. Brooks[3]) the leaves of a species of
Limnophila occurring in the Philippines yield about 0.2 p.c. of
an oil with a density of 0.850 and a rosemary-like odor.

Family: *ACANTHACEÆ.*

852. Oil of Strobilanthes lupulinus.

In an English journal[4]) mention is made of an oil that
was very probably obtained from *Strobilanthes lupulinus,* Nees
(*S. Dalzellii,* T. Anders), a plant that grows in enormous quan-
tities in the vicinity of Bombay. The oil distilled from the flower
buds had a strong agreeable odor and showed the following
properties: d 0.9648; $\alpha_D - 16°30'$; n 1.4688; A. V. 1.7; E. V. 257.

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[1]) Journ. Chem. Soc. 97 (1910), 1945.
[2]) Report of Schimmel & Co. April 1908, 121.
[3]) Philippine Journ. of Sc. 6 (1911), A, 346.
[4]) Perfum. Record 2 (1911), 96.

Family: RUBIACEÆ.

853. Gardenia Oil.

An oil was obtained from flowering gardenias[1]) according to the maceration process, by means of vaselin oil, with a yield of 0.0704 p.c. According to E. Parone[2]) it is yellow in color and at 20.5° has a specific gravity of 1.009; $[\alpha]_{D20°} + 1.47°$ in a 50 mm. tube. Under ordinary pressure it began to distill at 204° with partial decomposition, whereas under a pressure of 12 to 15 mm. it distilled largely between 84 and 150°. Parone identified the following constituents: *benzyl acetate, styrolyl acetate* (acetate of methyl phenyl carbinol $C_6H_5 \cdot CH \cdot [OCOCH_3]CH_3$) *linalool, linalyl acetate, terpineol* and *anthranilic acid methyl ester.*

Benzyl acetate is the principal constituent of gardenia oil, whereas the peculiar aroma is due primarily to the styrolyl acetate.

854. Oil of Chione glabra.

Origin. In the West Indian island Grenada, the tree *Chione glabra,* D.C. is known as *violette* on account of the aromatic odor of its flowers. In Porto Rico it is known *palo blanco.* The wood and bark possess a disagreeable fæcal odor which gradually disappears upon exposure.

Production and Properties. According to B. H. Paul and A. J. Cownley[3]) steam distillation of the bark yields a pale yellow volatile oil (yield 1.5 p.c.) that is heavier than water and which, when cooled to −20° congeals to a mass of needle-shaped crystals.

Composition. The oil, which possesses in a high degree the odor of the bark, has been examined by W. R. Dunstan and T. A. Henry[4]). It consists principally of a liquid substance, which congeals at low temperature, boils at about 160° (34 mm.), has

[1]) A number of species of the genus *Gardenia* (family *Rubiaceæ*) possess a very agreeable odor, e. g. *G. florida,* L., and *G. grandiflora,* Lour., which are cultivated in Germany as well as elsewhere for decorative purposes.
[2]) Boll. Chim. Farm. 41 (1902), 489; Chem. Zentralbl. 1902, II. 703.
[3]) Pharmaceutical Journ. 61 (1898), 51.
[4]) Journ. Chem. Soc. 75 (1899), 66.

a specific gravity of 0.850 at 15°, and the composition of which is expressed by the formula $C_8H_8O_2$. Its odor is aromatic and slightly fæcal. With acetic acid anhydride it yields an acetic ester melting at 88°. With hydroxylamine and phenylhydrazine there result compounds the formation of which indicates the presence of a carbonyl group. The oxime melts at 112°, the phenylhydrazone at 108°. Fused with potassium hydroxide, there results salicylic acid, also phenol, whereas nitric acid produces picric acid. These results indicate that the compound is o-*hydroxyacetophenone* $C_6H_4 \cdot OH^{[2]} \cdot CO \cdot CH_3^{[1]}$. As a matter of fact the synthetic preparation obtained from o-nitro cinnamic acid in a roundabout way agrees with the natural product.

Besides o-hydroxyacetophenone the oil contains a colorless, crystalline substance that melts at 82°. It is possibly an alkyl derivative of phenol, but could not be further investigated on account of the small amount available. In addition the oil contains traces of a nitrogenous substance, but it was not possible to establish the presence of indol or its derivatives which seemed indicated by the odor of the crude material.

855. Oil of Morinda citrifolia.

The fruits of the tropical *Morinda citrifolia*, L. contain, according to C. J. E. Lohmann[1]), a higher fatty acid, also an ester. From these fruits, known in Java as *bengkudu* or *tjangkudu*, A. W. K. de Jong distilled a volatile oil that was investigated by P. van Romburgh[2]).

The yellowish-colored oil had a specific gravity of 0.927 at 13° and was turbid in consequence of the separation of small crystals. Recrystallized from alcohol, these melted at 60° and consisted of *paraffin*, as was shown by analysis. The oil, deprived of crystals, dissolves almost completely in diluted caustic soda solution. The solution contained *caproic acid* (m. p. — 5.2°; $d_{15°}$ 0.932) and *caprylic acid* (m. p. 15.2°; $d_{14°}$ 0.913), also traces of a higher fatty acid.

In the neutral portion of the oil, which constituted only a small percentage thereof, there were identified, after saponifica-

[1]) Verslag's Lands Plantentuin, Buitenzorg 1896, 59.
[2]) Koninklijke Akademie van Wetenschappen te Amsterdam, 1909, 17.

tion, *ethyl alcohol* (characterized by its boiling point and the iodoform test), probably also *methyl alcohol,* and alcohols with an odor of fusel oil.

The fatty acids constitute more than 90 p.c., a remarkable phenomenon for a volatile oil.

856. Oil of Nuanua Leaves.

From the leaves of species of *Nelitris,* Gärtn., a tree known as *Nuanua,* which Schimmel & Co.[1] had obtained from Samoa, *steam* distillation yielded 0.63 p.c. of a yellowish-green oil with an ambra-like odor that had the following constants: $d_{15°}$ 0.9025; $\alpha_D + 9°30'$; $n_{D20°}$ 1.48490; A.V. 2.2; E.V. 7.4; soluble in about 8 vol. of 90 p.c. alcohol with the separation of slight amounts of paraffin.

The oil obtained by *water* distillation with a yield of 0.104 p.c. from the same material likewise had an ambra-like odor but was fainter and less agreeable than that of the oil obtained by steam distillation. $d_{15°}$ 0.9373; $\alpha_D - 10°10'$; $n_{D20°}$ 1.50142; A.V. 11.0; E.V. 11.0; soluble in about 12 vol. of 90 p.c. alcohol with sepa-ration of paraffin.

Family: CAPRIFOLIACEÆ.

857. Oil of Elderberry Flowers.

The oil of the flowers of *Sambucus nigra,* L., Ger. *Holunder,* has been prepared repeatedly both from fresh and dry material[2]. It was mostly obtained by shaking the aqueous distillate with ether after the water had been saturated with salt, and subsequent evaporation of the ether. In this manner Pagenstecher obtained 0.32 p.c. of oil. Schimmel & Co. obtained by steam distillation without the use of ether a yield of 0.0037 p.c. from fresh material and 0.027 p.c. from dry material.

Ordinarily the oil is of a butyraceous or wax-like consistence at medium temperature, of light yellow to yellowish-green color and of an intense elderberry blossom-like odor which becomes

[1]) Report of Schimmel & Co. November 1908, 136.

[2]) J. Eliason, Trommsdorff's Neues Journ. d. Pharm. 9 I. (1824), 246. — F. L. Winckler, Pharm. Zentralbl. 1837, 781. — Repertor. f. d. Pharm. 73 (1841), 35. — Müller, Arch. der Pharm. 95 (1846), 153.

especially pronounced in great dilution. More rarely is the oil liquid. It then congeals upon cooling (Winckler).

According to Gladstone[1]) it contains a terpene, $C_{10}H_{16}$. According to H. Haensel[2]), the stearoptene is a mixture of *palmitic acid* and *tricosane*, $C_{23}H_{48}$, a paraffin hydrocarbon.

According to E. Bourquelot and E. Danjou[3]) the leaves, buds and flowers contain a glucoside named *sambunigrin,* which emulsin hydrolyzes to benzaldehyde and hydrocyanic acid.

858. Oil of Sambucus Ebulus.

From the (fresh?) leaves of a dwarf elder, *Sambucus Ebulus*, L., Ger. *Zwergholunder,* or *Attich,* H. Haensel[4]) obtained 0.0763 p.c. of a dark brown oil with an unpleasant odor; $d_{15°} 0.8998$; A.V. 250.9; E.V. 46.0. Upon saponification it loses its unpleasant odor which is supplanted by a pleasant odor reminding of dry apricots and peaches. The oil contains *palmitic acid* and an *alcohol* not further characterized.

Family: VALERIANACEÆ.

859. Oil of Nardostachys Jatamansi.

According to Kemp[5]) the roots of *Nardostachys Jatamansi*, D.C. yield about 1 p.c. of a volatile oil of a light color: $d_{99°} 0.9748$; $\alpha_D - 19°5'$.

From the drug *Kan-sho-ko* which is esteemed in Japan as a perfume and which presumably consists of the rhizome of *Nardostachys Jatamansi*, D.C. to which are attached fragments of leaves, Y. Asahina[6]) obtained 1.9 p.c. of a greenish-yellow oil with a pleasant odor, which resinifies readily when exposed to the air: $d_{15°} 0.9536$; $\alpha_D - 11°30'$; $n_{D9°} 1.571$; A. V. 0; S. V. 45.7; S. V. after acetylation 66.42. It contains a *sesquiterpene* boiling between 250 and 254° ($d_{15°} 0.932$).

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[1]) Journ. Chem. Soc. 17 (1864), 1 *et seq.*; Jahresber. d. Chem. 1863, 545.

[2]) Pharm. Ztg. 50 (1905), 412.

[3]) Journ. de Pharm. et Chim. VI. 22 (1905), 154, 210, 219. — Comp. also Guignard, Compt. rend. 141 (1905), 16.

[4]) Apotheker Ztg. 25 (1910), 16.

[5]) Dymock, Warden and Hooper, Pharmacographia indica. Vol. II, 237.

[6]) Journ. Pharm. Soc. of Japan 1907, 355.

860. Oil of Valerian.

Oleum Valerianæ. — Baldrianöl. — Essence de Valériane.

Origin. *Valeriana officinalis*, L. and several of its varieties occur wild and cultivated in the temperate and more northern countries of Europe and Asia. The rhizomes contain a volatile oil with a peculiar odor which at an early time attracted attention and which caused the root to be used as a remedy. For purposes of commerce and distillation the plant is cultivated in Germany (Thuringia), France (Dép. du Nord), Holland, England and North America.

Production. For purposes of distillation the dry root is mostly used, rarely the fresh root. Whereas Trommsdorff claims that the dry root yields relatively more oil than the fresh root, Zeller points out that neither the fresh nor the dry condition of the root exercise any material influence on the yield. According to P. Carles[1]) the fresh root juice contains an oxydase which may exert some influence on the odoriferous constituents. Concerning the oil cells contained in valerian root see W. Unger, Apothcker Ztg. 27 (1912), 1021.

From the dry Thuringian root Schimmel & Co. obtained 0.5 to 0.9 p.c. of oil, from the Dutch about 1 p.c. The aqueous distillate is strongly acid from valéric acid which presumably results during the process of distillation upon hydrolysis of the bornyl valerate contained in the roots.

Properties. In the fresh condition, oil of valerian is a yellowish-green to brownish-yellow, limpid, slightly acid liquid of a penetrating, characteristic, not unpleasant odor. Old oils are dark brown and viscid, have a strong acid reaction and, on account of free valeric acid, a decidedly disagreeable odor. The stearoptene that occasionally separates from old oils consists of borneol.

As a rule the specific gravity lies between 0.920 and 0.960. Abnormally light were the oils investigated hy Oliviero (sec Composition). They had been distilled from fresh French roots of plants growing wild in the Départements Vosges and Ardennes. Their specific gravity is given as between 0.880 and 0.912 at 0°,

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[1]) Journ. de Pharm. et Chim. VI. 12 (1900), 148.

corresponding to a density of 0.868 to 0.900 at 15°; α_D – 8 to – 13°; $n_{D20°}$ 1.485; A. V. 14 to 50; E. V. 50 to 100. With 80 p.c. alcohol it yields a turbid solution and sometimes is insoluble; soluble in 0.5 to 1.5 vol. and more of 90 p.c. alcohol. Older oils are more readily soluble, in about 2 vol. and more of 80 p.c. alcohol.

Composition. Although valerian oil has been examined repeatedly since the beginning of the last century[1]), its composition has been ascertained only comparatively recently by the identification of its several constituents. This was done primarily by the investigations of G. Bruylants[2]) and Oliviero[3]).

Of the constituents of this oil *valeric acid,* which obtained its name from the plant, has been known the longest. It was also ascertained that the oil, upon oxidation, yielded ordinary camphor.

The lowest fraction of the oil consists of a mixture of l-*camphene*[4]) and l-*pinene.* According to Oliviero, there is present also a small amount of active citrene (?) although the proof of this statement is wanting.

Fraction 180° (ordinary pressure) of the saponified oil contains l-*borneol.* It is originally contained in the oil as ester of *formic, acetic, butyric* and *valeric acids,* however, by far the largest amount is combined with valeric acid. According to J. E. Gerock[5]) the oil contains about 9.5 p.c. bornyl valerate and 1 p.c. of bornyl ester of each of the other three acids.

[1]) J. B. Trommsdorff, Trommsdorff's Journ. d. Pharm. 18 1. (1809), 3 and Liebig's Annalen 6 (1833), 176 and 10 (1834), 213. — Ettling, *ibidem* 9 (1834), 40. — Gerhardt and Cahours, Annal. de Chim. et Phys. III. 1 (1841), 60. — F. Rochleder, Liebig's Annalen 44 (1842), 1. — C. Gerhardt, *ibidem* 45 (1843), 29 and Journ. f. prakt. Chem. 27 (1842), 124. — Pierlot, Annal. de Chim. et Phys. III. 14 (1845), 295 and 56 (1859), 291.

[2]) Berliner Berichte 11 (1878), 452.

[3]) Compt. rend. 117 (1893), 1096. — Bull. Soc. chim. III. 11 (1894), 150 and 13 (1895), 917.

[4]) The claim made by Oliviero that valerian oil and oil of spike are the first oils in which camphene was found is based on error. The occurrence of camphene in citronella oil and in ginger oil was reported in the *Report* of Schimmel & Co. for October 1893 pp. 15 and 25. The first publication of Oliviero (also that of Bouchardat on oil of spike) appeared in the December 23 number of the Comptes rendus for 1893.

[5]) Journ. d. Pharm. f. Elsaß-Lothringen 19 (1892), 82; Jahresb. f. Pharm. 1892, 445.

Fraction 132 to 140° (50 mm.) probably contains *terpineol*, which, however, could not be isolated in the crystalline condition. The formation of dipentene dihydrochloride admits, with fair certainty, to conclude the presence of this alcohol.

Between 160 and 165° (50 mm.) a lævogyrate sesquiterpene $C_{16}H_{24}$ and at 190° a substance passes over the analysis of which agrees with the formula $C_{16}H_{26}O$. Judging from its behavior toward benzoic acid anhydride and hydrogen chloride, this substance is an alcohol.

From the water that was used to wash the saponified oil, Oliviero separated an alcohol $C_{10}H_{20}O_2$ that crystallized in laminæ. It is strongly lævogyrate and melts at 132°. According to F. A. Flückiger[1]) the highest boiling fractions of valerian oil contain a blue oil boiling at 300°.

Merely on the strength of its elementary analysis, Bruylants[2]) is of the opinion that the liquid fraction distilling between 285 and 290° contains bornyl ether or bornyl oxide $C_{10}H_{17} \cdot O \cdot C_{10}H_{17}$. This, however, is not very probable and certain ly demands verification.

MEXICAN OIL OF VALERIAN.

A valerian root obtained by Schimmel & Co.[3]) from Mexico and presumably derived from *Valeriana Mexicana,* D.C. was distilled by them. However, only an aqueous distillate was obtained from which no oil separated. Only upon cohobation was an oily substance obtained which had the disagreeable odor of valeric acid and the specific gravity of which was 0.949 at 15°. It was optically inactive, and, when shaken with soda solution, it was dissolved with the exception of a few floccules. Titrated with alcoholic potassa the acid value was found at 415 corresponding to 89 p.c. of *valeric acid hydrate* $C_5H_{10}O_2 + H_2O$.

According to this observation Mexican valerian root yields next to no volatile oil but only free valeric acid. Inasmuch as the root has a decided odor of the acid it is to be assumed that valeric acid occurs in the root as such and is not formed during distillation.

[1]) Arch. der Pharm. 209 (1876), 204.
[2]) Berl. Berichte 11 (1878), 452.
[3]) Report of Schimmel & Co. April 1897, 44.

861. Kesso Root Oil.

Origin and Production. Japanese valerian root is not derived, as was at first assumed, from *Patrinia scabiosæfolia*, Link, but from *Valeriana officinalis*, L. var. *angustifolia*, Miq., a plant which is known in Japan as *Kesso Kanokosô*. Upon distillation it yields up to 8 p.c. of oil (mostly 5 to 6.5 p.c.) hence is much richer in oil than ordinary valerian root.

Properties. The lævogyrate oil can scarcely be distinguished from oil of valerian so far as the odor is concerned. It is heavier, *viz.*, $d_{15°}$ 0.960 to 1.004; α_D — 23 to — 34°; $n_{D20°}$ 1.477 to 1.487; A. V. 1 to 20; E. V. 92 to 134; E. V. after acetylation 145 to 157; soluble in 1 to 2.5 vol. and more of 80 p.c. alcohol, the dilute solution showing occasionally a faint opalescence.

Composition.[1]) Likewise as to its composition kesso oil closely resembles oil of valerian. In addition to practically all of the constituents of valerian oil it contains kessylacetate which is responsible for its high density. When distilled there first passes over a fraction which is strongly acid and has a most offensive odor of decaying cheese. It contains *acetic acid, valeric acid* and probably also *valeric aldehyde*.

Fraction 155 to 160° is strongly lævogyrate and, like the corresponding fraction of valerian oil, consists of l-*α-pinene* (m. p. nitrosopinene 101°) and l-*camphene*[2]) (m. p. of *iso*borneol 212°). Between 170 and 180° *dipentene* (m. p. of tetrabromide 123°) passed over. It is a question, however, whether this hydrocarbon is an original constituent of the oil or whether it has resulted from the action of acids on pinene or terpineol.

Like the *borneol* of oil of valerian, that of kesso oil is lævogyrate and is present as *acetic* and iso*valeric ester*. Bornyl formate present in oil of valerian is entirely wanting in kesso oil. *Terpineol* was identified by preparing dipentene dihydriodide, m. p. 76°, from fraction 200 to 220°. Other characteristic reactions for terpineol could not be obtained because of the presence of

[1]) J. Bertram and E. Gildemeister, Arch. der Pharm. 228 (1890), 483.
[2]) J. Bertram and H. Walbaum, Journ. f. prakt. Chem. II. 49 (1894), 18.

borneol which was difficult to remove. Fraction 260 to 280°, which had a decided sesquiterpene odor, yielded no solid hydrochloride. In addition to a blue oil, the highest fraction contains *kessyl acetate,* the acetate of an alcohol $C_{14}H_{24}O_2$.

Kessyl acetate, $C_{14}H_{23}O_2COCH_3$, is a viscid oil that does not solidify at — 20°. Under 15 to 16 mm. pressure it distills between 178 and 179°, under ordinary pressure at about 300° but not without decomposition; α_D — 70° 6′.

Kessyl alcohol, $C_{14}H_{24}O_2$, crystallizes in large, well-developed crystals of the rhombic system. It is odorless, insoluble in water, readily soluble in alcohol, ether, chloroform, benzene and petroleum ether. It melts at 85° and boils at 155 to 156° under 11 mm. pressure, and at 300 to 302° under ordinary pressure. Its alcoholic solution is lævogyrate.

Oxidized with potassium dichromate and sulphuric acid it is converted into a compound containing two hydrogen atoms less, that crystallizes in blunt needles, melts at 104 to 105° and deviates the ray of polarized light to the right.

The blue substance found in oil of valerian is also contained in kesso oil.

862. Oil of Valeriana celtica.

Valeriana celtica, L., a rather insignificant plant growing in the Alps of Styria, yields the drug formerly known as *Spica celtica,* Ger. *Speik, Alpenspik, celtischer Spik.* Upon distillation the root yields 1.5 to 1.75 p.c. of volatile oil with a strong odor reminding more of Roman chamomile and patchouly than of valerian. Its specific gravity is 0.967 and it boils between 250 and 300°[1]).

An oil, obtained by H. Haensel[2]) with a yield of 0.1 p. c., had an odor of valerian and asarum: $d_{20°}$ 0.9693; α_D — 42°; S. V. 62.5; E. V. of the previously saponified and acetylated oil 71.9; soluble in all proportions in 90 p. c. alcohol. It contains *palmitic acid* and a *sesquiterpene* boiling at about 255°; $d_{20°}$ 0.9359; α_D — 30.88°.

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[1]) Bericht von Schimmel & Co. October 1887, 36.
[2]) Chem. Zentralbl. 1909, II. 1557.

Family: COMPOSITÆ.

863. Ageratum Oil.

Ageratum[1]) *conyzoides*, L. is widely distributed in tropical countries, *e. g.* in Java[2]), in Central Africa[3]) and particularly in Annam[4]) where it is so common as to be a plague to the planters.

This plant was first distilled in Buitenzorg by P. van Romburgh[5]), who observed the occurrence of *methyl alcohol.* $d_{27.5°}$ 1.015; $a_D - 2.75°$. The oil distilled at about 260°, hence probably contains a derivative of the sesquiterpene series.

Another sample of oil, likewise from Java, had the following properties: $d_{15°}$ 1.028; $a_D - 1° 22'$; soluble in 1 vol. and more of 90 p. c. alcohol[6]).

For an ageratum oil obtained from Annam, Roure-Bertrand Fils[4]) record the following properties: $d_{15°}$ 1.1090; $a_D - 1° 20'$; A. V. 0.9; E. V. 11.2; almost completely soluble in 5 vol. and more of 80 p. c. alcohol, also in 0.5 vol. of 90 p. c. alcohol. The oil had been distilled with a yield of 0.0054 p. c.

864. Dog Fennel Oil.

Eupatorium capillifolium (Lam.), Small. (*E. fœniculaceum,* Willd.) is a North American *Eupatorium* that occurs from the Virginia coast regions southward. The common name dog fennel, Ger. *Hundefenchel,* is due to the fennel-shaped leaves.

An oil distilled in Florida from the entire plant was light in color and had an aromatic pepper-like odor, totally unlike fennel. $d_{15°}$ 0.935; $a_D + 17° 50'$. It contained a large amount of *phel-*

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[1]) According to H. Molisch and S. Zeisel *Ageratum mexicanum,* Sims (Berichte bot. Ges. 6 [1888], 353) in the fresh condition has an odor due in all probability to a volatile oil, whereas the dry plant has the odor of *cumarin,* 0.06 p. c. of which has been shown to be present. The leaves of *A. brachystephanum,* Reg. likewise contain cumarin after they are dead and dried.

[2]) Report of Schimmel & Co. April 1898, 53.

[3]) E. de Wildeman, *Notices sur les plantes utiles. Publication de l'État du Congo* 1906, Vol. II. Fasc. 1. p. 110.

[4]) Berichte von Roure-Bertrand Fils April 1914, 8.

[5]) Bericht von Schimmel & Co. October 1887, 36.

[6]) Observations made in the Laboratory of Schimmel & Co.

landrene[1]). A second oil, distilled from the flowering herb, yield 0.1 p.c., had the following properties: $d_{15°}0.926;$ $\alpha_D + 18°38';$ E.V. 7.11. It contained much phellandrene[2]). Whereas these oils were dextrogyrate, 30 samples distilled by E. R. Miller[3]) in the course of eleven years from material collected in Alabama were lævogyrate. The yield from fresh herb was 0.8 to 1.35 p.c.: $d_{25°}^{25°} 0.9278$ to 0.9472; $\alpha_D - 3.7$ to $- 16.8°;$ $n_{D20°} 1.50055$ to 1.50688; A.V. 0.18 to 0.25; S.V. 10.92 to 13.67; soluble in about 0.7 vol. of 90 p.c. alcohol, the addition of more solvent causing turbidity. The oil contained at most traces of aldehydes and ketones and possibly a little salicylic acid. A methoxyl determination revealed the presence of a phenol ether which proved to be the *dimethyl ether of thymohydroquinone* (b.p. 244°) and which constitutes the principal constituent of ·the oil. Acted upon with hydriodic acid it yielded thymohydroquinone (m.p. 142°) which could be oxidized to thymoquinone (m.p. 44 to 45°). Distilled with alcohol vapor, it was possible to separate a fraction that contained terpenes with low specific gravity (up to 0.8295 at 25°) and phellandrenes (m.p. of nitrosites 96 to 98°, 100 to 101° and 111 to 114°). The presence of neither pinene nor sabinene could be established. Linalool does not appear to be a constituent of the oil, but *borneol* is. It was characterized by oxidation to camphor (m.p. of oxime 116 to 117°). In the saponification liquor *acetic acid* (silver salt) was found, also other volatile acids.

865. Ayapana Oil.

Origin. *Eupatorium triplinerve*, Vahl (*E. Ayapana*, Vent.) is a native of equatorial America. It occurs wild in many other tropical countries and is cultivated in the East Indies, Mauritius, Mayotta and Réunion. Its leaves are used as Ayapana tea in disturbances of the digestive tract and diseases of the lungs. Upon distillation it yielded 1.14 p.c. of volatile oil[4]).

Properties[4]). Ayapana oil is light green in color and has a peculiar odor: $d_{15°} 0.9662$ to 0.9808; $\alpha_D + 2°55'$ to $+ 6°;$

[1]) Report of Schimmel & Co. April 1896, 64.
[2]) *Ibidem* April 1904, 96.
[3]) Bulletin of the University of Wisconsin No. 693. Madison (Wisc.) 1914, p. 7.
[4]) Report of Schimmel & Co. April 1907, 106; April 1908, 17.

n_D 1.50882[1]); A.V. 5.5 (one determination); E.V. 5.9 to 8.0; E.V. after acetylation 23.4 (one determination); soluble in $1^1/_2$ to $4^1/_2$ vol. and more of 90 p.c. alcohol. Upon distillation under 3.5 mm. pressure 57.4 p.c. passed over from 40 to 104°, 28 p.c. between 104 and 105°, 15.9 p.c. remaining in the residue[2]). Of another oil that was distilled under 12 mm. pressure, 8 p.c. passed over between 55 to 116°, 80 p.c. between 116 and 119°, and 12 p.c. between 119 and 123°[1]).

Composition. According to F. W. Semmler[1]) the principal fraction of the oil consisted of a mixture of an oxygenated substance and a sesquiterpene. In order to obtain the former in a pure condition the fraction was heated with sodium, distilled at 118° (12 mm.) and subsequently treated with permanganate until the color of the solution no longer disappeared. The substance thus obtained had the composition $C_{12}H_{18}O_2$ and otherwise the following properties: b.p. 118° (12 mm.); $d_{20°}$ 0.9913; $\alpha_D + 0°$; n_D 1.51339; mol. refr. found 58.88, computed for $C_{12}H_{18}O_2/_2$ 57.42. Inasmuch as the stability of this substance towards sodium indicated an ether, it was subjected to a treatment with hydrogen iodide and red phosphorus and thereby converted to hydrothymoquinone (b.p. 150 to 160° under 12 mm. pressure; m.p. 143°), which was further characterized by oxidation to thymoquinone (m.p. 48°; m. p. of monoxime 160 to 161°). As an intermediate product, the monomethylether, $C_{11}H_{16}O_2$ (b.p. 117 to 130° under 12 mm. pressure; $d_{20°}$ 1.0111; n_D 1.5188) had resulted. Hence the *dimethylether of hydrothymoquinone* is the principal constituent of the oil. Up to that time its only occurrence was that observed by O. Sigel[3]) in arnica root oil.

Probably the oil also contains small amounts of cumarin. Although the fresh plant is almost odorless, when dried it has the characteristic odor of cumarin and melilotic acid. E. Heckel[4]), who has made the observation that anæsthetics have the capacity to liberate cumarin from fresh plants, found that when fresh ayapana plants are treated with ethyl chloride the odor becomes

[1]) Berl. Berichte 41 (1908), 509.
[2]) Report of Schimmel & Co. April 1907, 106; April 1908, 17.
[3]) Liebig's Annalen 170 (1873), 345.
[4]) Compt. rend. 152 (1911), 1825.

apparent after 5 to 6 minutes, when treated with ethyl ether and chloroform after about 15 minutes.

866. Oil of Eupatorium serotinum.

From the herb of *Eupatorium serotinum,* Mchx., which grows in the eastern part of the United States of North America, E. R. Miller[1]) obtained 0,51 p.c. of oil (computed with reference to herb not fully dried); $d_{25°}$ 0.9075; α_{D} lævogyrate; $n_{\text{D}24°}$ 1.4990; A.V. 0.5; S.V. 28.7; S.V. after acetylation 61.92; soluble in 0.5 vol. of 90 p.c. alcohol, the addition of 1.7 vol. caused turbidity. The oil was of a rather dark color, so that an exact determination of its optical rotation was not possible. Apparently it contains traces of salicylic acid and for the most part consists of *sesquiterpenes.*

867. Liatris Oil.

According to W. F. Henry[2]), the leaves of *Liatris spicata,* Willd. contain 0.09 p.c. of volatile oil. On account of its *cumarin* content, which, however, is lower than in *L. odoratissima,* Willd., apparently successful cultural experiments[3]) have been made in the botanical garden of Marseilles.

Liatris odoratissima, Willd. (dog's tongue, hound's tongue, vanilla, Ger. *Hirschzunge, Hundszunge*) occurs in large amounts in isolated places in the savannahs of North Carolina to Florida. The leaves when fresh have but a slight odor of cumarin and vanillin which, however, develops strongly when they are dried. They are used against moths and as a perfume in tobacco. W. Procter[4]) showed the presence of cumarin which, for a time, was prepared on a large scale. From 1 lb. of dry leaves Th. F. Wood[5]) obtained 2 to 2.5 drachms (0.78 to 0.98 p.c.) of

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[1]) Bulletin of the University of Wisconsin No. 693, Madison (Wisc.) 1914, p. 38. — According to the same author either no oil or but traces could be obtained from the herb of *Eupatorium purpureum, E. hyssopifolium* and *E. perfoliatum.* From the roots of *E. aromaticum,* L., C. H. Blouch (Americ. Journ. Pharm. 62 [1890], 124) obtained upon distillation with water 0.8 p.c. of volatile oil.

[2]) Americ. Journ. Pharm. 64 (1892), 603.

[3]) Parfum. moderne 3 (1910), 77.

[4]) W. Procter jun., Americ. Journ. Pharm. 31 (1859), 556; Jahresber. d. Chem. 1860, 486; Pharm. Zentralbl. 1860, 896.

[5]) Pharmaceutical Journ. III. 12 (1882), 764.

pure cumarin. In addition the leaves contained a substance with a very unpleasant and persistent odor, *liatrol*.

The acclimatization of this plant in Marseilles was not· successful [1]).

868. Grindelia Oil.

From the dry herb of *Grindelia robusta,* which is a native of the western United States, H. Haensel [2]) obtained upon distillation 0.288 p.c. of oil with a strong and not unpleasant odor: $d_{15°}$ 0.9582; a_D (calculated from the alcoholic solution) $- 8°8'$; S.V. 75.1; S.V. after acetylation 162.1. It contains 8 p.c. of a brown, phenol-like oil, also *borneol.*

869. Oil of Solidago odora.

Origin. The genus *Solidago* is represented in the United States of North America by not less than 75 species, of which about 50 occur east of the Rockies, and are all known as golden-rod. Many of these plants possess more or less aromatic properties and some of them are so plentiful in certain regions as to be regarded as weeds.

Solidago odora, Ait. is known as sweet-scented goldenrod or Blue Mountain tea. It is found from New Hampshire south to Florida and westward to Missouri and Texas. Upon distillation it yields about 1 p.c. of oil, occasionally less (down to 0.64 p.c.) or more (up to 1.53 p.c.) [3]). For the most part the commercial oils are not pure but distillates from *Solidago odora* mixed with other herbs [4]).

Properties. The odor of the oil is strongly aromatic reminding of anise and safrol, but not particularly agreeable. $d_{15°}$ 0.94 to 0.96 [5]); $a_D + 9° 20'$ to $+ 13° 12'$; n_D 1.506 to 1.514; S.V. 7 to 9; S.V. after acetylation 19.4; soluble in 0.4 vol. of 90 p.c. alcohol [3]).

Composition. The oil has been examined by E. R. Miller and J. M. Moseley [3]). The presence of *methyl chavicol* was proven

[1]) Parfum. moderne 3 (1910), 77.

[2]) Apotheker Ztg. 18 (1903), 499. — Chem. Zentralbl. 1907, I. 1332.

[3]) Journ. Americ. Chem. Soc. 37 (1915), 1286.

[4]) Report of Schimmel & Co. April 1906, 62; October 1906, 72.

[5]) *Ibidem* October 1891, 51.

by its oxidation to anisic acid (m.p. 184°) and homoanisic acid (m.p. 85 to 86°). The methyl chavicol content amounted to about ·76 p.c. (methoxyl determination). Anethol was not present. Phenols, aldehydes and ketones are also absent. The presence of *α-pinene* is doubtful. The hydrocarbon yielded a nitrosochloride melting at 103°, but its nitrolamine bases had melting points that did not agree with those of the known ones. The phellandrene test gave negative results. Neither could the presence of camphor be proven. *Borneol,* however, was identified by its melting point (203 and 204°) and its phenyl urethane (m.p. 138 to 139°). In addition to borneol another alcohol seems to be present in the oil. In the saponification liquor there are presumably three volatile *acids* and one non-volatile acid.

870. Oil of Solidago canadensis.

The fresh, flowering herb of *Solidago canadensis*, L. yields 0.63 p.c. of oil of a light yellow color and a very pleasant, sweetish aromatic odor. $d_{15°}$ 0.859; $\alpha_D - 11° 10'^1$).

The oil contains about 85 p.c. terpenes. *Pinene* is the principal hydrocarbon. *Phellandrene* and *dipentene* and possibly limonene are also present. The higher boiling fractions consist of *borneol, bornyl acetate* and *cadinene.* Quantitative determinations revealed a total of 9.2 borneol, of which 3.4 p.c. is present as acetate. It is noteworthy how closely related chemically this goldenrod oil is to the pine needle oil of a totally different family.

871. Oil of Solidago rugosa.

Solidago rugosa, Mill. grows in moist places from New-foundland westward to Ontario and south to the Gulf of Mexico. The fresh herb yields[2]) 0.4 p.c. of a volatile oil ($d_{25°}^{25°}$ 0.8620; $\alpha_D - 12° 8'$; $n_{D28°}$ 1.4813; S.V. 4.22; S.V. after acetylation 10.97), which boils between 165 and 180° and apparently consists principally of l-*α-pinene,* as indicated by the formation of a nitrosochloride. The constants of the higher fractions suggest the presence also of d-*limonene* and *β-pinene.*

[1]) Report of Schimmel & Co. April 1894, 57; April 1897, 46.

[2]) E. R. Miller and J. M. Moseley, Journ. Americ. Chem. Soc. 37 (1915), 1285.

872. Oil of Solidago nemoralis.

Schimmel & Co.[1]) describe an oil of *Solidago nemoralis,* · Ait., that had been sent to them from North America. Its color was light olive-green, its odor peculiar, reminding somewhat of cypress oil: $d_{15°}$ 0.8799; α_D −23°10′; E. V. 14.4; E. V. after acetylation 38.2. With 7 vol. and more of 95 p.c. alcohol it formed only a turbid solution.

More recently an oil was examined by E. R. Miller and M. H. Eskew[2]), which had been distilled in October from flowering herb with a yield of 0.322 p.c.: $d_{25°}^{25°}$ 0.8532; α_D −16.17°; $n_{D18°}$ 1.47397; soluble in about 4 vol. of 90 p.c. alcohol and in about 27 vol. of 70 p.c. alcohol; S.V. 5.6; S.V. after acetylation 9.4. Miller and Eskew found about 0.6 p.c. of *phenols* and *α-pinene* as principal constituents. This hydrocarbon showed an angle of rotation α_D −19.37°, whence the authors conclude that it is a mixture of l- and d-*α-pinene.* It was characterized by the preparation of its nitrosochloride and its nitrolpiperidide (m. p. 118 to 119°). Phellandrene could not be found, neither borneol although the camphor-like odor which resulted upon the oxidation of a borneol fraction seemed to indicate the presence of this alcohol. The detection of camphor was unsuccessful, but that of *salicylic acid,* by shaking the oil with 3 p.c. potassium hydroxide solution, was successful. It gave the color reaction with ferric chloride and when acted upon with methyl alcohol and sulphuric acid produced the well-known odor of methyl salicylate. The saponification liquid contained *acetic acid* (silver salt).

873. Erigeron Oil.

Oleum Erigerontis. — Erigeronöl. — Essence d'Erigeron.

Origin. *Erigeron canadensis,* L., is a very common weed which occurs especially in the American peppermint fields. It ·is known as fleabane, horseweed or butterweed. Upon distillation the fresh herb yields 0.33[3]) to 0.66[4]) p.c. of oil, the dry

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[1]) Report of Schimmel & Co. April 1906, 62.
[2]) Journ. Americ. Chem. Soc. 36 (1914), 2538.
[3]) Report of Schimmel & Co. October 1894, 72.
[4]) F. Rabak, Pharm. Review. 23 (1905), 81; 24 (1906), 326.

herb only 0.26[1]) p.c. In the United States the oil finds medicinal application to a limited extent.

Properties. When fresh, oil of erigeron is colorless or light yellow and limpid. It has a peculiar aromatic odor reminding somewhat of caraway, and a biting taste. Exposed to the air it resinifies rapidly and becomes more viscid and darker. Occasionally crystals separate from the oil[1]). $d_{15°}$ 0.8565 to 0.868[2]); $\alpha_D + 52°$[2]) to $+ 83°$[1]); A. V. 0; E. V. 39 to 108; E. V. after acetylation 67 to 108. At times the oil dissolves in an equal volume of 90 p.c. alcohol, frequently however, the solution remains turbid even after the addition of several volumes of solvent.

Composition. Erigeron oil distills over almost completely at 175°[3]) and consists for the most part of d-*limonene*. By passing hydrogen chloride into the oil a dihydrochloride[4]) melting at 47 to 48°[5]) results. With bromine a tetrabromide melting at 104 to 105°[6]) was obtained. For its further characterization F. W. Meissner[7]) prepared the nitrosochloride and from the α-nitrosochloride the benzylamine base melting at 90 to 92°.

From fraction 205 to 210° Hunkel[8]) prepared a nitrosochloride the piperidide of which melted at 159 to 160° and hence may be regarded as terpineol nitrolpiperidide. The second constituent of erigeron oil, therefore, is *terpineol*.

874. Oil of Blumea balsamifera.

Origin and Production. In India the half shrub-like *Blumea balsamifera,* D.C., is indigenous from the Himalaya to Singapore also in the Malay Archipelago, *e. g.,* the Philippines[9]). It also

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[1]) F. Rabak, Pharm. Review **23** (1905), 81; **24** (1906), 326.

[2]) Report of Schimmel & Co. October 1894, 72.

[3]) F. B. Power, Pharm. Rundsch. (New York) **5** (1887), 201.

[4]) Vigier and Cloez, Journ. de Pharm. V. **4** (1881), 236.

[5]) F. Beilstein and E. Wiegand, Berl. Berichte **15** (1882), 2854.

[6]) O. Wallach, Liebig's Annalen **227** (1885), 292.

[7]) Americ. Journ. Pharm. **65** (1893), 420.

[8]) E. Kremers, Pharm. Rundsch. (New York) **13** (1895), 137.

[9]) R. F. Bacon, Philippine Journ. of Sc. **4** (1909), A, 127; Report of Schimmel & Co. October 1909, 180.

grows in Burma[1]), Tonkin[2]), China and in the islands Hai-nan and Formosa.

In Hai-nan, also in the Chinese province Kwang-tung this plant is distilled for the production of the so-called Ngai camphor, *Ngai-fên*, which is obtained in considerable amounts. From Hoi-han, on the island of Hai-nan, 15000 lbs. are said to be exported annually. The crude Ngai camphor is rectified in Canton and is then known as *Ngai-p-'ien*[3]). In the south of China about 15000 to 18000 lbs. are produced, which however are used for domestic consumption[4]). In Burma also this camphor is produced[5]).

In China the Ngai camphor is used for ritual purposes also medicinally. Further, it is added to the finer grades of so-called India ink.[6]).

The volatile oil is contained in the stems and leaves. R. F. Bacon[7]), who recommended the production of the oil in the Philippines, says that the yield is 0.1 to 0.4 p.c.; Cayla[2]) gives 0.25 p.c. Experiments made by the Indian Forest Department are said to have given 1.88 p.c.[8]).

Properties and Composition. In 1895 Schimmel & Co. secured a sample of Ngai camphor, which consisted of a yellowish-white crumbly crystalline mass that was almost pure l-*borneol*[9]). The identity of Ngai camphor with lævogyrate borneol had previously been recognized by S. Plowman[10]) and by F. A. Flückiger[11]).

[1]) V. Cayla, Journ. d'Agriculture tropicale 9 (1909), 251.

[2]) *Ibidem* 8 (1908), 30; Report of Schimmel & Co. April 1908, 150.

[3]) E. M. Holmes, Pharmaceutical Journ. III. 21 (1891), 1150.

[4]) Journ. d'Agriculture tropicale 13 (1913), 317.

[5]) Buchner's Neues Repert. f. d. Pharm. 23 (1874), 321; Hanbury, Science Papers, 1876, p. 394.

[6]) Flückiger, *Pharmakognosie*. III. ed. Berlin 1891, p. 158; Flückiger and Hanbury, Pharmacographia. London 1879, p. 518.

[7]) R. F. Bacon, Philippine Journ. of Sc. 4 (1909), A, 127; Report of Schimmel & Co. October 1909, 180.

[8]) Perfum. Record 3 (1912), 341.

[9]) Report of Schimmel & Co. April 1895, 76.

[10]) Pharmaceutical Journ. III. 4 (1874), 710. — Neues Repert. f. d. Pharm. 23 (1874), 325.

[11]) Pharmaceutical Journ. III. 4 (1874), 829.

In Buitenzorg[1]) an oil had been obtained from the leaves of *Blumea balsamifera* the specific gravity of which was 0.944 at 28°.

Some years ago Schimmel & Co. came into possession of a Ngai camphor oil with a borneol-like characteristic odor from which probably the bulk of the borneol had been separated by steam distillation.

This oil, examined by R. Jonas[2]), had the following properties: $d_{15°}$ 0.950; $\alpha_D - 12°30'$; $n_{D20°}$ 1.48151; A. V. 23.35; E. V. 1; E. V. after acetylation 198 (corresponding to 63.95 p. c. of alcohol $C_{10}H_{18}O$). Fractionation under diminished pressure yielded as first fraction a small amount of an oil boiling from 28° (40 mm.) to 80° (30 mm.). In it, also in the following fraction, the presence of *cineol* could be demonstrated by means of the iodol addition product melting at 111.5°. The next fraction ($\alpha_D + 4°10'$) which boiled between 80° (30 mm.) and 75° (12 mm.) yielded a nitroso-chloride melting at 103.5°. Judging from the boiling point of this fraction it is probable that the nitrosochloride was that of *limonene*. Inasmuch as further fractionation was rendered difficult by the separation of borneol crystals, the separation of this substance by freezing became necessary. Previously, however, the oil was shaken with soda solution to remove traces of two solid acids, probably *palmitic* and *myristic acids*, and with 5 p.c. sodium hydroxide solution to remove phenols. The crystals that separate upon cooling from the oil deprived of acids and phenols, represent a mixture of l-*borneol* and l-*camphor*. For the isolation of the borneol a part of this mixture was heated with phthalic acid anhydride in an autoclave for 6 hours to 110°. The acid phthalate was dissolved in dilute soda solution and, after the alkaline solution had been shaken with ether it was distilled with steam after addition of caustic soda. The borneol, which is readily volatile with steam, separated in the receiver in the form of laminar crystals melting at 203°. The residue from the ether solution yielded, with hydroxylamine, camphor oxime melting at 118 to 119°. The oil deprived of borneol and camphor consisted for the most part of *sesquiterpenes* and *sesquiterpene alcohols*. Purified by steam distillation it boiled in the neighborhood of 280°.

[1]) Verslag 's lands plantentuin Buitenzorg 1895, 38.

[2]) Report of Schimmel & Co. April 1909, 147.

The phenol separated from the oil by sodium hydroxide solution melted at 82 to 83° and upon elementary analysis yielded results corresponding with the formula $C_{10}H_{12}O_4$. More careful investigation revealed that it was the *dimethyl ether of phloracetophenone* first prepared by P. Friedländer and L. C. Schnell[1]) from the trimethylether of phloroglucinol and later examined more carefully by S. von Kostanecki and J. Tambor[2]). As shown by the method of preparation, the following structural formula is assigned to this substance: —

$$
\begin{array}{c}
\text{CH} \\
\text{H}_3\text{CO}\cdot\text{C}\diagup\quad\diagdown\text{COH} \\
\text{HC}\diagdown\quad\diagup\text{C}\cdot\text{CO}\cdot\text{CH}_3 \\
\text{C}\cdot\text{OCH}_3
\end{array}
$$
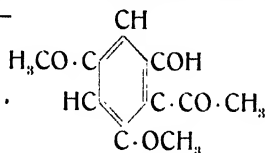
Of the derivatives of this phenol the following were prepared: the acetyl compound (m. p. 106 to 107°), a bromide $C_{10}H_{11}O_4Br$ (m. p. 187°), its condensation product with benzaldehyde, the 2-hydroxy-4.6-dimethylchalkone (m. p. 91 to 92°) and its acetyl derivative (m. p. 130°).

The trimethylether (m. p. 103°) obtained from the dimethylether of phloracetophenone was oxidized with 3.3 p.c. permanganate solution at water-bath temperature to a keto acid $C_{11}H_{12}O_6$. It melted at 155.5° giving off carbon dioxide and carbon monoxide. The oxime melted at 88.5 to 93°.

In a Ngai camphor distilled in Dehra Dun, India, by R. S. Pearson from the air-dried leaves, Schimmel & Co.[3]) found about 75 p.c. of l-*camphor* and 25 p.c. l-*borneol* together with minimal traces of a yellowish oil: The crude product revealed a specific angle of rotation $[\alpha]_D — 46.26°$ in 54.18 p.c. xylene solution and had a melting point 175°. The same xylene solution, after acetylation, yielded a saponification value of 46.4, corresponding to 13.2 p.c. of borneol. This amounts to 24.4 p.c. borneol in the Ngai camphor itself. The separation of the two constituents was accomplished in the usual manner by converting the borneol into the acid phthalic ester and driving over the camphor with water vapor.

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[1]) Berl. Berichte 30 (1897), 2152.

[2]) *Ibidem* 32 (1899), 2262.

[3]) Report of Schimmel & Co. April 1910, 148.

How it comes about that Ngai camphor consists at times exclusively of *l*-borneol, and at times of a mixture of *l*-borneol and *l*-camphor, has not yet been explained. Possibly this may be attributed to the material used. In this connection it should be mentioned that *Blumea lacera,* D.C. yields a similar camphor (see below).

875. Oil of Blumea lacera.

Blumea lacera, D.C. is a perennial of India, which has a strong camphor-like odor, and which, on this account, is used by the natives against flies and other insects.

From 150 lbs. of fresh flowering herb, W. Dymock[1]) obtained upon distillation about two ounces (0.085 p.c.) of a light yellow oil: $d_{26.7^\circ}$ 0.9144; α_D — 66°.

According to V. Cayla[2]) the plant is known in Burma as *Kadu* and upon distillation yields more blumea camphor than *B. balsamifera.*

876. Oil of Pluchea fœtida.

According to F. Rabak[3]), the fresh herb of *Pluchea fœtida,* D.C. (*P. camphorata,* D.C.), which is a native of the southern United States of North America, yields 0.025 p.c. of a pale golden-yellow volatile oil: d 0.9329; α_D — 10.8°; n_{D23° 1.4845; A.V. 4.1; E.V. 44; E.V. after acetylation 104. It is soluble in an equal volume of 80 p.c. alcohol, but the addition of 5 vol. and more of solvent causes turbidity. Of its constituents *cineol* was identified by means of its iodol derivative melting at 113°.

877. Oil of Sphæranthus indicus.

According to W. Dymock[1]), *Sphæranthus indicus,* L., which has a rose-like odor and which is used extensively in India for medicinal purposes, yields an oil that has a dark red color, is viscid and is relatively soluble in water. From 150 lbs. of fresh herb about $1/2$ oz. (0.022 p.c.) of oil were obtained.

[1]) Pharmaceutical Journ. III. 14 (1884), 985.

[2]) Journ. d'Agriculture tropicale 9 (1909), 252.

[3]) Midland Drugg. and pharm. Review 45 (1911), 485.

878. Oil of Helichrysum Stoechas.

The oil from the flowering plant *Helichrysum Stœchas*, D.C. is used in Spain as a remedy against bladder and kidney troubles. Its odor is that of low-grade coniferous distillates; about $^3/_4$ boils between 155 and 170° and $^1/_4$ between 170 and 260°. $d_{15°}$ 0.873. *α-Pinene*[1]) is probably the principal constituent.

879. Oil of Helichrysum arenarium.

From the flowers of *Helichrysum arenarium,* D.C. (*Gnaphalium arenarium,* L.) H. Haensel[2]) obtained 0.04 p.c. of a dirty green oil with a benumbing strongly aromatic odor, which, upon evaporation of the oil, reminded distinctly of celery: $d_{90°}$ 0.921; A.V. 14.45; S.V. 9. At 20° a solid substance separated. It contains a *stearoptene* that melts at 48 to 50 and is insoluble in alcohol, an *acid* melting at 34 to 36° and a small amount of a *phenol,* presumably *p*-cresol.

880. Oil of Helichrysum saxatile.

According to L. Francesconi and R. Sernagiotto[3]), *Helichrysum saxatile,* Moris contains an oil with a peculiar pungent odor which, however, reminds of roses: d 0.9020; $α_D$ —11.71°; n_D 1.4769. Aldehydes and phenols are absent. It distills for the most part about 240° and apparently contains a substance belonging to the hydroaromatic series, possibly an oxygenated sesquiterpene derivative.

881. Oil of Helichrysum angustifolium.

Helichrysum angustifolium, D.C. (*H. italicum,* G. Don) is a fragrant herb widely distributed in southern Europe where it covers large areas. Thus it grows in masses on Monte Portofino, near Genoa, also in Hungary and Dalmatia.

From dry herb Schimmel & Co.[4]) obtained 0.075 p.c. of oil: $d_{15°}$ 0.892 to 0.920; $α_D$ +4° 25' to — 9° 40'; $n_{D20°}$ 1.4745 to 1.4849;

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[1]) Bericht von Schimmel & Co. October 1889, 54.

[2]) Chem. Zentralbl. 1910, II. 1538.

[3]) Gazz. chim. ital. 44 (1914), II. 419; Chem. Zentralbl. 1915, I. 835.

[4]) Report of Schimmel & Co. October 1903, 73; April 1909, 57; October 1911, 54; April 1914, 65.

A.V. up to 15; E.V. 39 to 134; soluble in 9 to 10 vol. of 90 p.c. alcohol, occasionally with the separation of paraffin.

According to Heine & Co.[1]) the oil is rich in *nerol* (see vol. I. p. 362), partly as ester, partly free.

882. Oil of Elecampane.

Oleum Helenii. — Alantöl. — Essence de Racine d'Aunée.

Origin and Production. Upon distillation of the comminuted root of *Inula Helenium,* L. with water vapor 1 to 3 p.c. of a solid, crystalline mass results that is permeated with little liquid oil. This is known as elecampane oil. As such it is scarcely used for any other purpose than the preparation of alantolactone, the heleniine of C. Gerhardt[2]).

Properties. Normal elecampane oil with its full alantolactone content is a mass of colorless needles, saturated with little brown oil, that melts to a brown liquid at about 30 to 45°. The odor is peculiar and reminds somewhat of labdanum[3]). $d_{30°}$ (in the molten condition 1.015 to 1.038; $\alpha_D +123°45'$ (one determination); $n_{D20°}$ 1.52208 (one determination); A.V. 6 to 8; E.V. 160 to 180; E.V. after acetylation 199 (one determination).

In connection with oils that had been deprived in part of their alantolactone, the following values were ascertained[4]): $d_{15°}$ 1.015 to 1.043; $\alpha_D +91°40'$ (one determination); $n_{D20°}$ 1.5141 to 1.5233; A.V. 10 to 24; E.V. 135 to 168; E.V. after acetylation 160 to 182; soluble in 1 vol. of 90 p.c. alcohol either clear or with turbidity, the addition of more solvent causing opalescence or even turbidity.

Composition. Elecampane oil consists almost completely of *alantolactone* with which are admixed small amounts of *alantolic acid, alantol* and a substance named *helenin* by Kallen[5]), and

[1]) Germ. Pat. 209382; Chem. Zentralbl. 1909, I. 1785.

[2]) Ann. de Chim. et Phys. II 72 (1839), 163 and III. 12 (1844), 188. — Liebig's Annalen 34 (1840), 192 and 52 (1844), 389.

[3]) Report of Schimmel & Co. April 1912, 60.

[4]) *Ibidem* April 1915, 17.

[5]) Berl. Berichte 6 (1873), 1506. Comp. also Kallen, *Über Alantolacton und die Anlagerung von Blausäure an ungesättigte Lactone. Inaug.-Dissertation.* Rostock 1895. J. Bredt and W. Posth (Liebig's Annalen 285 [1895], 349) suggest that the name helenin be dropped since it applies to no less than three different substances.

which J. Spring[1]) named iso*alantolactone*. For details see vol. I, p. 523.

Alantic or alantolic acid, to which alantolactone corresponds, has the formula $C_{14}H_{20} \diagdown^{OH}_{COOH}$. Its salts are formed when alantolactone is heated with alkalies. The acid crystallizes in small needles and melts at 94° giving off water. It is likewise readily soluble in alcohol and ether. Heated with water it is largely decomposed. From the hot aqueous solution it separates in small crystals upon cooling. These consist of alantic acid admixed with lactone. Because of the ease with which the one is converted into the òther, crude elecampane oil contains alantic acid as well as alantolactone.

Alantol is an oil that boils in the neighborhood of 200° and occurs in but very small amount. Moreover, it appears to occur only in very fresh elecampane root. It is a yellowish liquid and an isomer of ordinary camphor, $C_{10}H_{16}O$. Distilled with phosphorus pentasulphide it yields cymene $C_{10}H_{14}$, boiling at 175°.

The highest boiling fractions of the oil contain a blue substance.

883. Oil of Inula viscosa.

Inula viscosa, Ait., is a plant, sticky to the touch, which is distributed over the entire Riviera and fills the air with its resinous, balsamic odor. In popular medicine the fresh leaves are used against snake bite. In Eubœa the fresh herb is added to wine, probably in order to impart to the latter the desired resinous taste. Upon distillation of the herb, Schimmel & Co.[2]) obtained 0.062 p.c. of a dark brown, viscid oil with an unpleasant odor. $d_{25°}$ 1.006; A.V. 164.63; E.V. 15.77. At ordinary temperature *paraffin* is separated abundantly. The fatty acids isolated were liquid.

From Algerian herb Roure-Bertrand Fils[3]) distilled an oil with a light brown color, and an odor that reminded of hyssop as well as of eucalyptus oil. $d_{15°}$ 0.9436; $\alpha - 24°0'$; soluble in 1 vol. and more of 80 p.c. alcohol with the separation of paraffin.

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[1]) Arch. der Pharm. **239** (1901), 201.

[2]) Report of Schimmel & Co. October 1903, 76.

[3]) Berichte von Roure-Bertrand Fils April 1911, 23.

With 10 vol. of 70 p.c. alcohol the solution remained somewhat turbid. About 70 p.c. of the oil was taken up by 50 p.c. resorcinol solution, hence *cineol* may be regarded as the principal constituent of the oil.

884. Oil of Inula graveolens.

Upon steam distillation[1] *Inula graveolens* (L.), Desf., which is widely distributed throughout the Mediterranean countries, yields a brown oil with a greenish fluorescence. $d_{15°}$ 0.9754; α_D - 36° 40'; $n_{D20°}$ 1.47597; A.V. 8.45; E.V. 161.3; E.V. after acetylation 239.38; soluble in 3 to 3.5 vol. and more of 70 p.c. alcohol with a decided separation of paraffin. Judging by its odor the oil contains bornyl acetate.

885. Oil of Osmitopsis asteriscoides.

An alcoholic infusion of *Osmitopsis asteriscoides* (L.), Cass. (*Osmites Bellidiastrum*, Thbg., *Bellidiastrum osmitoides,* Less.), which grows abundantly on Table Mountain of South Africa, is used in Cape Colony as a remedy against lameness.

The volatile oil of this plant has been examined by E. von Gorup-Besanez[2]. It was limpid and of a yellowish-green color. The odor was not pleasant, reminding both of camphor and cajuput oil; $d_{16°}$ 0.931.

The oil began to boil at 176°, two-thirds passing over between 178 and 188°, the remainder between 188 and 208°. When the thermometer had risen to 206°, the neck of the retort showed a slight deposit of crystals, presumably *camphor.*

Fraction 178 to 182° had the formula $C_{10}H_{18}O$, as shown by analysis, and in all probability consisted of *cineol,* already indicated by odor and specific gravity.

886. Oil of Parthenium argentatum.

The Mexican *Parthenium argentatum,* Gray contains according to P. Alexander[3] 8 to 10 p.c. (computed with reference to

[1] Report of Schimmel & Co. April 1905, 82.

[2] Liebig's Annalen 89 (1854), 214.

[3] Berl. Berichte 44 (1911), 2320.

dry material) of caoutchouc, so-called Guayule caoutchouc of commerce, and about 0.5 p.c. of volatile oil.

For the preparation of this oil Alexander used Mexican material which probably had been collected and dried only a short time before shipment. It yielded about 0.015 p.c. of a greenish-yellow, slightly lævogyrate oil[1]) ($d_{15°}$ 0.8861) which consisted exclusively of hydrocarbons. Under 17 mm. pressure 30 p.c. boiled between 50 and 60°, 20.3 p.c. between 60 and 80° and 24.8 p.c. between 120 and 160°. The residue amounted to 5.5 p.c. Of its constituents l-α-*pinene* was identified (m.p. of nitrosochloride 100 to 102°; m.p. of nitrolbenzylamine 122°). The odoriferous constituent of the oil reminds of pepper: b.p. 130 to 140° (17 mm.); $d_{15°}$ 0.9349; $[α]_{D16°}$ −21°24'; $n_{D16°}$ 1.496. Alexander assumes that it is a *sesquiterpene* but was unable to identify it with any of the known hydrocarbons of this group.

Another oil that had been distilled from material which had been stored for a longer period, proved to contain considerable oxygenated material and, upon distillation, left a resinous residue of 50 p.c.

In closing, Alexander states that the oil of *Parthenium argentatum* bears a close resemblance to German chamomile oil. To what extent the odor of the two oils may be similar cannot be judged; as to their chemical composition, however, they are very different.

887. Oil of Ambrosia artemisiæfolia.

Ambrosia artemisiæfolia, L., is a rather common weed in North America and is known as ragweed, hog weed, bitterweed and Roman wormwood.

Fresh, flowering herb yields upon distillation 0.07 p.c. of a deep green oil, with an aromatic, not unpleasant odor. $d_{15°}$ 0.870; $α_D$ −26°[2]).

A distillate from Florida (yield 0.15 p.c.) had the following properties[3]): $d_{15°}$ 0.876; $α_D$ −1°; E.V. 7.94; with an equal volume of 90 p.c. alcohol, the oil yields a clear solution, which becomes turbid upon the addition of more solvent.

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[1]) The poor yield was due to the fact that no suitable apparatus for distillation on a large scale was available.

[2]) Report of Schimmel & Co. October 1894, 70.

[3]) *Ibidem* April 1904, 99.

888. Oil of Spilanthes oleracea.

From the ethereal extract of *Spilanthes oleracea,* Jacq., Ger. *Parakresse,* E. Gerber[1]) obtained by steam distillation 0.27 p.c. of an oil with the following properties: d 0.847; $\alpha_D +1.85°$. It has a sharp taste and for the most part distills between 135 and 190° (35 mm.). The principal fraction (b.p. 145 to 155°), consists essentially of a hydrocarbon $C_{15}H_{30}$, *spilanthene.* Purified by means of oxidation with permanganate at water bath temperature it boils at 135 to 138° (25 mm.) or 220 to 225° (ordinary pressure); d 0.845. Bromine, in chloroformic solution, produces a thick oil of the composition $C_{15}H_{30}Br_2$. An acid isolated from the oxidizing mixture melted at 180°. It crystallizes from water and yields crystalline precipitates with silver nitrate and copper sulphate. The barium salt is amorphous.

889. Santolina Oil.

Origin. *Santolina Chamæcyparissus,* L. which is indigenous to southern Europe and which is frequently cultivated in gardens, is characterized by a strong, penetrating, aromatic odor. On account of its therapeutic properties it was formerly official and is today still used as a popular remedy. Thus it is used against cramps and as an anthelmintic.

From herb obtained from Turin, Schimmel & Co.[2]) obtained 0.47 p.c. of oil. According to L. Francesconi and P. Scaraffia[3]) the yield varies, according to the stage of development of the plant, between 0.198 and 1.15 p.c., being highest shortly before the flowering period. The composition of the oil also varies according to the same conditions. With the aid of such reagents as osmic acid, ferric chloride and dilute Sudan-III-solution, these investigators showed that the oil is located principally in the epidermal tissues.

Properties. The oil prepared by Schimmel & Co.[2]) was dark brown in color and its odor reminded somewhat of wormwood and tansy. $d_{15°}$ 0.9065; $n_{D20°}$ 1.50040; A.V. 6.6; E.V. 16.4;

[1]) Arch. der Pharm. 241 (1903), 270.

[2]) Report of Schimmel & Co. October 1911, 108.

[3]) Atti R. Accad. dei Lincei, Rome (5), 20 (1911), II. 255, 318, 383; Chem. Zentralblatt 1912, I. 344, 345.

E. V. after acetylation 74.2; the optical rotation could not be determined on account of the dark color. The oil was soluble in 0.5 vol. and more of 90 p.c. alcohol with the separation of paraffin. In 80 p.c. alcohol it was not soluble. Francesconi and Scaraffia found: $d_{15°}$ 0.8732; $[\alpha]_{D25°}$ —11.74°.

Composition. The lowest fractions contain a terpene (b.p. 165 to 170°) and probably a phenol ether. With hydroxylamine hydrochloride the oil yields an oxime and a hydroxylaminoxime. The underlying ketone is named *santolinenone* by Francesconi and Scaraffia and has been further investigated by Francesconi and N. Granata[1]). Thus is became apparent that it consisted of a mixture of two unsaturated ketones $C_{10}H_{16}O$, α- and β-*santolinenone*, and a third saturated *ketone* $C_{10}H_{18}O$, of the type of camphor. α-Santolinenone is optically inactive but represents a racemic mixture as was proven by breaking up the α-santolinenone hydroxylaminoxime (m.p. 190°) into its optically active components by means of d-camphor sulphonic acid. β-Santolinenone is also inactive and probably racemic. Its hydroxylamine derivative melts at 62°. The third ketone is lævogyrate and yields a dextrogyrate oxime melting at 116 to 117°. According to Francesconi, Granata and A. Sanna[2]) the d-camphor sulphonate of the l-hydroxylaminoxime of α-santolinenone melts at 192 to 196°; $[\alpha]_D$ —20.35°. The l-hydroxylaminoxime melts at 171°; $[\alpha]_D$ —115.7°.

The action of diluted acids on the hydroxylaminoxime did not, as was expected, regenerate the ketone, but the hydroxylaminoxime behaves analogous to pulegone hydroxylaminoxime[3]). Judging by the abnormal refraction and by the comparison of the hydroxlamine derivatives with those of pulegone, the authors assume the correctness of the formula of α-santolinenone put up by them.

$$C:CH_2$$
$$H_2C \diagup \quad \diagdown CO$$
$$H_2C \diagdown \quad \diagup CH_2$$
$$CH \cdot CH(CH_3)_2$$
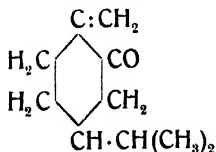
α-Santolinenone.

[1]) Gazz. chim. ital. 44 (1914), II. 150; Chem. Zentralbl. 1914, II. 1439.
[2]) Gazz. chim. ital. 44 (1914), II. 354; Chem. Zentralbl. 1915, I. 788.
[3]) Gazz. chim. ital. 45 (1915), I. 35, 167; Chem. Zentralbl. 1915, I. 1117, 1313.

When α-santolinenone hydroxylaminoxime is heated in alcoholic solution, α-santolinenone aminoxime (m. p. 155°) is formed, also α-santolinenone dioxime (m. p. 260°). A better yield of dioxime is obtained when the hydroxylaminoxime is heated with alcohol and mercuric oxide. Continued heating of α-santolinenone hydroxylaminoxime with dilute hydrochloric acid yields a compound $C_{10}H_{16}N_2$ (a nitrilimine?) melting at 119 to 120°, and α-santolinenone iminoxime, melting at 169 to 172°. The latter compound does not always result, at times its place is taken by α-santolinenone imine.

890. Roman Chamomile Oil.

Oleum Chamomillæ Romanæ. Oleum Anthemidis. — Römisch Kamillenöl. — Essence de Camomille Romaine.

Origin and Production. *Anthemis nobilis,* L., the so-called Roman chamomile, occurs wild in western and southern Europe, in Great Britain, France, Spain and Portugal and is cultivated in Germany, England and Belgium, mostly the double form in which the inflorescence consists entirely of ray florets. The plants are propagated mostly by the division of the roots, rarely by seeds. Cultural experiments are reported by E. Senft[1]).

The oil of Roman chamomile is produced principally in England, more particularly in Croydon, Mitcham, Carshalton, Sutton and Long Melford. The yield from the entire plant, which is mostly employed, varies between 0.2 and 0.35 p. c., the flower heads yield up to 1 p. c. Upon distillation of the dry, double flowers (*Anthemis nobilis, flore pleno,* D.C.) the drug proper, Schimmel & Co.[2]) obtained in one instance as much as 1.75 p. c. In an experiment to ascertain whether the common, single variety with ray florets, or the one without ray florets (*Anthemis nobilis,* var. *β-floscula,* Pers.) is richer in oil, the same firm[2]) obtained 0.33 p. c. from the former and 0.3 p. c. of oil from the latter.

Properties. Freshly distilled Roman chamomile oil has a light blue color, which under the influence of light and air

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[1]) Zeitschr. f. d. landw. Versuchsw. in Österreich, 1914, Fascicles 3/4. Mitteilungen des Komitees zur staatlichen Förderung der Kultur von Arzneipflanzen in Österreich No. 17, p. 23.

[2]) Report of Schimmel & Co. April 1915, 39.

gradually changes to green and finally brownish-yellow. The odor of the oil is strong and pleasant, the taste burning. $d_{15°}$ 0.905 to 0.918; α_D — 2° 30′ to +3°.

The optical rotation has been determined but rarely since the ordinary lamps do not afford sufficient light because of the dark color of the oil. In this case[1]) the sodium lamp constructed by E. Beckmann[2]) may be employed as source for light. It is fed with salt dust supplied by the electrolysis of sodium hydroxide or sodium carbonate. $n_{D20°}$ 1.442 to 1.457; A.V. 1.5 to 14; E.V. 214 to 317. For its solution 6 to 10 vol. of 70 p.c. alcohol are required, turbidity resulting occasionally; 1 to 2 vol. or more of 80 p.c. alcohol are sufficient, but with this solvent turbidity likewise results occasionally with separation of paraffin.

Composition. *Angelic acid,* without doubt, is the principal constituent of Roman chamomile oil, in which it was discovered in 1848 by C. Gerhardt[3]) and thereby became readily accessible. The other statements made by Gerhardt about the occurrence of angelic aldehyde and a terpene boiling at 175°, "chamomillene", later proved to be wrong.

E. Demarçay[4]) showed that angelic acid does not occur free in the oil but combined with *butyl* and *amyl alcohols.* He thought that he had found valeric acid as a second acid, but this also later investigations proved to be wrong.

More detailed studies of the oil were made by R. Fittig and H. Kopp[5]); also by Fittig and J. Köbig[6]). Kopp saponified the oil and determined the acids thus obtained, whereas Köbig resolved the unsaponified oil into fractions and studied these. These two supplementary investigations revealed the presence of a number of new substances. 1. An ester of iso*butyric acid* boiling at 147 to 148°. (It was supposed to be the *iso*butyl ester but this has not been verified.) 2. *Angelic acid butyl ester.*

[1]) Report of Schimmel & Co. April 1915, 39.

[2]) Berl. Berichte 45 (1912), 2523.

[3]) Compt. rend. 26 (1848), 225. — Ann. de Chim. et Phys. III. 24 (1848), 96. — Liebig's Annalen 67 (1848), 235. — Journ. f. prakt. Chem. 45 (1848), 321.

[4]) Compt. rend. 77 (1873), 360; 80 (1875), 1400.

[5]) Berl. Berichte 9 (1876), 1195; 10 (1877), 513.

[6]) Liebig's Annalen 195 (1879), 79, 81 and 92.

3. *Angelic acid* iso*amyl ester*. 4. Ester of tiglinic acid (resulting from inversion during the investigation. See below). 5. An ester of an *hexyl alcohol* which upon oxidation yielded caproic acid. 6. From the lowest boiling portions, 150 to 160°, from which the alcohols had been removed, a white amorphous powder was separated, which, though it was not isolated in a pure condition, consisted of *methylacrylic acid* $CH_2 : C \big\langle \begin{smallmatrix} CH_3 \\ COOH \end{smallmatrix}$ judging by its properties. Hence the original oil probably contains an ester of this acid. 7. Fraction 213.5 to 214.5° constituted a colorless liquid with a camphor-like odor, which could not be distilled completely under ordinary pressure without decomposition. According to analysis this alcohol has the formula $C_{10}H_{16}O$, and was named *anthemol*. Its acetic ester boils at 234 to 236°. Saponification of the ester regenerates the original alcohol. Chromic acid oxidizes anthemol completely, dilute nitric acid oxidizes it to *p*-toluic acid and terephthalic acid. In addition there resulted a third, more readily soluble acid, possibly terebinic acid.

These basal researches have been supplemented by others and partly corrected.

Thus, E. E. Blaise[1]) has been able to show that the tiglinic acid observed by Fittig and Kopp is not an original constituent of the oil, but has resulted from the action of alkali or heat on angelic acid. According to Blaise, the saponification of 500 g. of oil at ordinary temperature yielded 190 g. crude acid. Of this 90 g. were *angelic acid* and 25 g. iso*butyric acid,* whereas considerable amounts of polymethylacrylic acid remained in the residue as colorless powder when the acids were distilled. The neutral products of saponification consisted of 25 g. iso*amyl alcohol,* 80 g. *active hexyl alcohol,* 33 g. *anthemol* and 30 g. *normal butyl alcohol,* which was characterized by its boiling point and its phenyl urethane melting at 55 to 56°. This is contrary to the observations of Köbig[2]) who supposed that he had found *iso*butylalcohol.

P. van Romburgh[3]) has proven that the caproic acid under consideration is identical with *methylethylpropionic acid* and that

[1]) Bull. Soc. chim. III. 29 (1903), 327.

[2]) Liebig's Annalen 195 (1879), 79, 81 and 92.

[3]) Recueil trav. chim. des P.-B. 5 (1886), 219 and 6 (1887), 150; Berl. Berichte 20 (1887), Referate 375 and 468.

the hexyl alcohol, which has also been prepared synthetically, is
$\begin{matrix} C_2H_5 \\ CH_3 \end{matrix}$$>$CH·CH$_2$·CH$_2$OH. The *methylethylpropyl alcohol* of Roman
chamomile oil boils at 154°, has a specific gravity of 0.829 and
is dextrogyrate ($[\alpha]_D + 8.2°$), whereas the synthetic alcohol is
inactive. The amount of hexyl alcohol contained in the oil is
about 4 p.c.

The highest boiling fractions contain a blue constituent, the
cœrulein or *azulene* (comp. Chamomile oil p. 623).

It should be mentioned that L. Naudin[1]) isolated from Roman
chamomile flowers by extraction with petroleum ether a paraffin
$C_{18}H_{36}$, *anthemene,* melting at 63 to 64°. According to T. Klobb,
J. Garnier and R. Ehrwein[2]) this substance melts at 64° and has
the composition $C_{30}H_{62}$. It is known that paraffins are found in
larger or smaller amounts in flower oils such as those of rose,
neroli, German chamomile, arnica, &c. Hence it may be assumed
that the anthemene is a constituent of Roman chamomile oil, a
suspicion supported by the behavior of the oil toward alcohol (see
Properties). Proper treatment of the oil ought to result in the
isolation of this hydrocarbon.

891. Oil of Anthemis Cotula.

Distillation of the fresh flowers of *Anthemis Cotula,* L. and
extraction of the aqueous distillate with ether, yielded G. E. Hurd[3])
0.013 p.c. of oil. The entire fresh plant yielded, when treated
in like manner, 0.01 p.c. of a reddish oil with an acid reaction
and a bitter taste, $d_{26°}$ 0.858. Upon cooling a crystalline acid
separated which, after purification, melted at 58°. The same acid
was obtained upon saponification of the oil. The saponified oil
boiled between 185 and 290° and left a residue of 20 p.c.

892. Oil of Milfoil.

The *fresh flowers* of *Achillea Millefolium,* L., milfoil, Ger.
Schafgarbe, yield, upon distillation, 0.07 to 0.25 p.c. of volatile

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[1]) Bull. Soc. chim. II. 41 (1884), 483; Jahresber. d. Chem. 1884, 526.

[2]) *Ibidem* IV. 7 (1910), 940.

[3]) Americ. Journ. Pharm. 57 (1885), 376.

oil. *Dry* flowers as a rule do not yield more although the herb loses about 50 p.c. water[1]). In one instance dry flowers yielded 0.485 p.c.[2]). The oil has a deep blue color and a strongly aromatic, camphor-like odor. The specific gravity of the oil distilled in Germany lies between 0.900 and 0.925 at 15°. A. Sievers[1]) observed 0.8687 to 0.8935 in connection with his own distillation of American oils; A. B. Aubert[3]), on the other hand, d_{22} 0.9217. The optical rotation was observed once[2]) in a solution in absolute alcohol (1 : 200) in a 50 mm. tube as — 1.65°. A.V. 1 to 12; E.V. 19 to 27; S.V. of American oils[1]) 29.3 and 37.3; E.V. after acetylation 66 to 79; soluble in 0.5 to 1 vol. of 90 p.c. alcohol, occasionally with the separation of paraffin.   •

Of the constituents of the oil, which was first prepared by L.F. Bley[4]), Schimmel & Co.[5]) identified *cineol*. The acid component of the esters is, in part, *acetic acid*[1]). The high-boiling blue constituent of the oil may be identical with the azulene or cœrulein of chamomile oil.

From the *roots* of milfoil Bley[6]) obtained 0.032 p.c. of an almost colorless oil with an unpleasant taste and a peculiar odor reminding faintly of valerian. The aqueous distillate contained acetic acid. The roots contain traces of a volatile sulphur compound.

893. Iva Oil.

Origin. *Achillea moschata*, L., the herb of which is used in the manufacture of the well-known iva liqueur[7]), grows in the highest Alps and owes its agreeable odor to a volatile oil, of which the dry, flowering herb yields 0.3 to 0.6 p.c.[8]).

Properties. The oil is rarely yellow or green in color, mostly greenish-blue to dark blue. Its odor is strongly aromatic and

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[1]) A. Sievers, Pharm. Review 25 (1907), 215.

[2]) H. Haensel, Pharm. Ztg. 47 (1902), 74.

[3]) Journ. Americ. Chem. Soc. 24 (1902), 778; Chem. Zentralbl. 1902, II. 798.

[4]) Trommsdorff's Neues Journ. d. Pharm. 16, II. (1828), 96.

[5]) Report of Schimmel & Co. October 1894, 38.

[6]) Trommsdorff's Neues Journ. d. Pharm. 16, I. (1828), 247.

[7]) Formerly the herb of *Ajuga moschata*, Schreb. was official in the French Pharmacopœia as *Herba Ivæ moschatæ*. V. F. Kosteletzky, *Allgem. med.-pharm. Flora*, Prague 1833, p. 777.

[8]) Comp. H. Haensel, Apotheker Ztg. 15 (1900), 271.

somewhat narcotic reminding of valeric aldehyde, cineol and thujone. $d_{15°}$ 0.928 to 0.959; α_D — 12° 30' to — 14° 47' (two determinations); $n_{D20°}$ 1.47607 (one determination); A. V. 5 to 21; E. V. 18 to 44; E. V. after acetylation 91.5 and 115.4 (two determinations); soluble in about 1 vol. and more of 80 p.c. alcohol, as a rule with the separation of paraffin.

Composition. Of its constituents the following have been identified: *cineol* (iodol reaction)[1]), an *aldehyde* (valeric aldehyde?)[2]), *l-camphor* (m.p. of semicarbazone 237.5°)[2]) and *palmitic acid*[3]). As revealed by the acetylation, alcohols also are present.

The so-called *"ivaol"* of the supposed composition $C_{24}H_{40}O_2$ which A. von Planta-Reichenau[4]) obtained by fractionation cannot have been a chemical individual as shown by the wide range of boiling temperature, *viz.* 170° to 210°.

894. Oil of Achillea nobilis.

The oils from the flowers, herb and seeds of *Achillea nobilis,* L., Ger. *Edelschafgarbe,* were distilled by L. F. Bley[5]). Dry flowers yielded 0.24 p.c., dry herb 0.26 p.c., and the seeds 0.19 p.c. of volatile oil. The oil from the herb had a specific gravity of 0.970. Its odor was strong, camphor-like, similar to that of milfoil, but finer, and its taste was spice-like bitter.

An oil examined by P. Echtermeyer[6]) was distilled from the flowering herb. $d_{15°}$ 0.9363; α_D — 10.41°; ester content computed as $C_{10}H_{17}O \cdot COCH_3$ 18.2 p.c.; ester content of the acetylated oil 34.3 p.c. *Borneol* was identified (m.p. 203°; m.p. of urethane 139°; m.p. of bromine addition product 104 to 105°) also *camphene* (conversion into *isoborneol*). A *hydrocarbon* $(C_{10}H_{16})_n$, boiling between 240 and 245°, is also present.

From the saponification liquid, acid liberated a small amount of a *phenol* the odor of which reminded of thyme, which did not solidify at — 15° and which, with ferric chloride, yielded a grayish-

[1]) Report of Schimmel & Co. October 1894, 31.
[2]) *Ibidem* April 1912, 83.
[3]) H. Haensel, Chem. Zentralbl. 1907, II. 1620.
[4]) Liebig's Annalen 155 (1870), 148.
[5]) Arch. der Pharm. 52 (1835), 124.
[6]) *Ibidem* 243 (1905), 238.

green color. Of acids, *formic, acetic* and caprinic (?) were shown to be present.

895. Oil of Achillea coronopifolia.

From Spain Schimmel & Co.[1]) obtained a deep blue, limpid oil of *Achillea coronopifolia,* Willd. Its strong odor was agreeable and reminded of tansy. $d_{15°}$ 0.924.

896. Oil of Achillea Ageratum.

The oil of *Achillea Ageratum,* L. was prepared by S. de Luca[2]) from the flowering plant. $d_{24°}$ 0.849.

Distillation yielded two fractions. The first boiled between 165 and 170°; the second between 180 and 182° and upon analysis yielded results corresponding with the formula $C_{26}H_{44}O_3$.

897. Oil of Tagetes patula.

The flowers of *Tagetes patula,* L., a native of Mexico, is frequently cultivated in European gardens and was formerly official in Europe under the wrong name of *Flores africani*. Upon distillation of the *fresh* flowering heads with their bracts, Schimmel & Co.[3]) obtained a yield of 0.1 p.c. The oil has a golden-yellow color and an aromatic, strong taste which reminds somewhat of fruit esters and olefinic terpenes. $d_{15°}$ 0.8856; α_D —5°35′; $n_{D20°}$ 1.49714; A.V. 2.0; E.V. 18.7; E.V. after acetylation 74.3; soluble in about 6 vol. and more of 90 p.c. alcohol with opalescence.

The *dried* inflorescences of the same harvest were also subjected to distillation[4]). The yield amounted to 0.08 p.c. computed with reference to the fresh material and 0.57 p.c. computed with reference to the dry material. The oil was brownish-yellow and differed but little from that obtained from the fresh flowers. $d_{15°}$ 0.8925; α_D —9°; $n_{D20°}$ 1.49938; A.V. 6.4; E.V. 10.6; soluble in 9 to 10 vol. of 90 p.c. alcohol with turbidity, miscible with 95 p.c. alcohol.

Similar properties were shown by oils obtained by both water and steam distillation of air-dried stems and leaves, with a yield

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[1]) Report of Schimmel & Co. April 1898, 72.

[2]) Annal. de Chim. et Phys. V. 4 (1875), 132; Jahresber. d. Chem. 1875, 849.

[3]) Report of Schimmel & Co. November.1908, 141.

[4]) *Ibidem* April 1909, 87.

of 0.07 p.c. (computed with reference to fresh herb), and 0.218 p.c. respectively (computed with reference to dry herb). $d_{15°}$ 0.9034; $\alpha_D + 1°15'$; $n_{D20°}$ 1.49938; A. V. 14; E. V. 12.4 (heated again E. V. 10.6); did not yield a clear solution with 10 vol. of 90 p.c. alcohol, miscible with 95 p.c. alcohol. From the saponification liquid a fatty acid was obtained which, after several recrystallizations, melted at 62° *(palmitic acid).*

According to the physiological investigation of J. Pohl, of Prague, the oil does not possess any specific action[1]).

898. Oil of German Chamomile.

Oleum Chamomillæ. — Kamillenöl. — Essence de Camomille[2]).

Origin. The common chamomile, *Matricaria Chamomilla*, L. (*Chrysanthemum Chamomilla,* Bernh.) grows throughout Europe, with exception of the extreme north. It has migrated to North America and Australia where it has become common.

Production. For the distillation of chamomile oil, which is at times designated German chamomile oil in order to distinguish it from Roman chamomile oil, the less perfect flowers which are less suited for sale as drug, also the siftings consisting of individual disk florets are used. The material best suited for distillation of the oil comes from Hungary. The yield amounts to 0.2 to 0.38 p.c. On account of their low oil content, chamomile was formerly distilled with lemon oil, yielding the former *Oleum Chamomillæ citratum* of the drug shops.

A. Jama[3]) has ascertained that the volatile oil of chamomile is localized at two different places. The hollow floral disk contains a ring of collateral fibrovascular bundles, the phloem of which is preceded by schizogenous secretory cells. On the fruit receptacle and on the floral tubes are oil-secreting hairs consisting of two rows of cells, the type of glands being characteristic of the composites.

Jama distilled both oils separately. From 4 kg. of pure florets he obtained 14 g. oil = 0.35 p.c. and from 1 kg. of pure

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[1]) Report of Schimmel & Co. April 1910, 102.

[2]) In England and North America the designation Oil of Chamomile implies that of *Anthemis nobilis.*

[3]) Apotheker Ztg. 24 (1909), 585.

floral disks he obtained 5.1 g. oil $= 0.51$ p.c. The oil from the florets revealed the well-known deep blue color, that from the disks was faintly green and after a few days had become yellow. At ordinary temperature both oils were viscid.

Properties. At middle temperatures chamomile oil is a somewhat viscid liquid of deep blue color. Stored carelessly, with exposure to light and air, the color changes to green and finally turns brown. The odor of the oil is strong and characteristic, the taste bitter and aromatic. $d_{15°}$ 0.922 to 0.956. Inasmuch as some oils are rather viscid even at $15°$ and begin to separate crystals the determination of the density must at times be made in the undercooled condition. Cooling to a lower temperature causes the oil to become butyraceous and at $0°$ it congeals to a fairly firm mass. A.V. 9 to 50; E.V. 3 to 33; E.V. after acetylation 117[1]) and 155 (two determinations); soluble in 95 p.c. alcohol but mostly only with separation of paraffin.

Jama has ascertained the constants of the oils obtained from the separate parts of the inflorescences. For the oil from the florets he found: $d_{15°}$ 0.954; $\alpha_D \pm 0°$; $n_{D21°}$ 1.363734; S.V. 74.4; for the oil from the disks: $d_{15°}$ 0.949; $\alpha_D \pm 0°$; $n_{D21°}$ 1.363716; S.V. 33.7.

Composition. Disregarding some of the less important constituents, comparatively little is known about the composition of oil of chamomile. The older investigations of Bornträger[2]) and G. Bizio[3]) produced little worth mentioning.

The investigation of J. H. Gladstone[4]) was restricted principally to the blue constituent named *cœrulein*. His statements concerning the properties, behavior and composition of this substance differ considerably from those made by S. Piesse[5]) as well as those made by J. Kachler[6]).

An oil distilled by Kachler began to boil at $105°$. Up to $180°$ 4.5 p.c. passed over. This fraction had a faint blue color and a

[1]) H. Haensel, Chem. Zentralbl. 1907, I. 1332.

[2]) Liebig's Annalen 49 (1844), 243.

[3]) Wiener akadem. Berichte 43 (1861), 2. Abtlg., 292; Jahresber. d. Chem. 1861, 681.

[4]) Journ. Chem. Soc. 17 (1864), 1 *et seq.*; Jahresber. d. Chem. 1863, 550.

[5]) Compt. rend. 57 (1863), 1016; Chem. News 8 (1863), 245, 273; Chem. Zentralbl. 1864, 320.

[6]) Berl. Berichte 4 (1871), 36.

strong odor of chamomile. 8.3 p.c. distilled over between 180 and 250°. Between 255 and 295° 42 p.c. passed over in the form of handsome blue vapors. The distillate collected above 295° (25 p.c.) was very viscid and the vapors finally became violet. 20 p.c. remained as a pitchy, brown mass. The distillation was accompanied by decomposition for all of the fractions had an acid reaction. By shaking them with aqueous potassa an acid was removed the analysis of the silver salt of which yielded results corresponding with *caprinic acid,* $C_{10}H_{20}O_2$ (H. Haensel[1]) believes the oil to contain *nonylic acid*). Repeated fractionation of the two lower fractions, after they had been freed of acid, yielded an oil boiling between 150 and 165°, the composition of which agreed by chance with the formula $C_{10}H_{16}O$. However, it cannot be assumed that a fraction boiling within a 15 degree limit is a chemical unit. The analyses of the subsequent fractions, also representing mixtures, are therefore devoid of interest.

The blue oil named *azulene* by Piesse boiled between 281 and 289°. Kachler regarded it as a polymer of camphor of the formula $(C_{10}H_{16}O)_3$. Treated with potassium there resulted a hydrocarbon boiling between 250 and 255° to which there was assigned the formula $C_{30}H_{18}$ which is not rendered probable by the low boiling point. Phosphorus pentoxide abstracts water from the blue oil with the formation of a hydrocarbon $(C_{10}H_{14})_n$. The entire behavior of the blue fraction of chamomile oil agrees completely with that of the deep blue oil obtained by P. Mössmer[2]) by the dry distillation of galbanum resin. Presumably the high-boiling blue fractions of many other oils, such as milfoil, kesso, valerian, Roman chamomile, wormwood &c. are identical with that of chamomile oil. However, no other oil is colored so intensely as the latter, hence it may be contained in the purest condition in chamomile oil.

As a result of the examination of their spectra A. Tschirch[3]) has arrived at the conclusion that the blue fractions of volatile oils are closely related.

[1]) Chem. Zentralbl. 1907, I. 1332.

[2]) Liebig's Annalen 119 (1861), 262.

[3]) *Die Harze und die Harzbehälter.* II. ed., vol. I, p. 378; A. Tschirch and M. Hohenadel, Arch. der Pharm. 223 (1895), 278.

A. E. Sherndal[1]) who has recently investigated azulene
assumes, without further ado, the identity of these blue sub-
stances. Azulene is soluble in strong mineral acids and separates
unchanged from their solution upon the addition of water. He
shook 50 g. of an intensely blue fraction of an oil, the name of
which he does not mention, with 10 g. of 83 p.c. sulphuric acid
and set the mixture aside over night. The acid layer was then
separated, diluted with water and treated with benzin until the
latter was no longer colored blue. The benzin solution was
shaken with 85 p.c. phosphoric acid until the blue color had
disappeared. The acid layer, colored dark red, was separated,
diluted with water and extracted with ether whereby he obtained
0.141 g. (0.28 p.c.) of blue oil. In like manner Sherndal obtained
larger amounts of azulene, which was finally purified by distil-
lation in vacuum. In thin layers azulene shows a deep blue
color, in thicker layers it appears black. Its odor is faintly
phenol-like reminding somewhat of thymol. Elementary analysis
and molecular weight determination in benzene agreed with the
formula $C_{15}H_{18}$. Exposed to the air it resinifies quickly. B. p. 295
to 300° (ordinary pressure) with partial decomposition, 185 to
195° (25 mm.); d_{25}. 0.9738. It is soluble in most organic solvents.
The solution in 60 to 65 p.c. sulphuric acid is yellow and fluoresces
strongly. The solution in phosphoric acid fluoresces with a reddish-
yellow and apple-green color. From the acid solution, benzin
does not take up azulene, hence sesquiterpenes can be readily
removed. Heating with 94 p.c. sulphuric acid on a water bath
does not change azulene. Action of nitric acid on the glacial
acetic acid solution converts azulene into a yellow, amorphous
mass. Oxidation with potassium permanganate yielded no charac-
teristic "Abbau" products. Treatment with acetic acid anhydride
and sulphuric acid resulted in a water-soluble substance, probably
a sulphonic acid.

According to later investigations by the same author[2]),
azulene readily yields a picrate that is well suited to its identi-
fication and purification. To a solution of 1 g. of picric acid in
20 cc. of 95 p.c. alcohol Sherndal added a solution of 1 g.

[1]) Journ. Americ. Chem. Soc. 87 (1915), 167.
[2]) Ibidem 1537.

azulene in 5 cc. alcohol. Within a few minutes the entire solution solidified to a crystalline mass, which was redissolved upon heating. From this solution the picrate again separated upon cooling in short, black crystal needles. It melted at 118°. In order to ascertain the composition of this picrate it was heated with a definite amount of barium hydroxide and water. Titration of the excess of barium hydroxide revealed that the picrate is composed of one molecule of azulene and one molecule of picric acid.

Upon reduction with colloidal palladium-hydrogen, azulene takes up eight atoms of hydrogen with the formation of a colorless hydrocarbon $C_{15}H_{26}$ which possesses the properties of a bicyclic dihydrosesquiterpene and is probably identical with dihydro-α-gurjunene. $d_{20°}$ 0.8935; $n_{D20°}$ 1.490; $\alpha_D + 0°$. This reduced azulene gives an intense color reaction with acetic acid anhydride + sulphuric acid, also with bromine and acetic acid.

The reduction of azulene shows that it is closely related to the sesquiterpenes. It contains four double bonds and is tricyclic. Moreover, the ready formation of a picrate suggests the presence of an aromatic nucleus. Conjugated hydroaromatic double bonds are wanting for it cannot be reduced with sodium and alcohol. The blue color must be explained by the peculiar arrangement of the double bonds in the azulene molecule.

The congealing of chamomile oil at low temperatures is caused by its paraffin content. The *paraffin,* which remains as a dark-colored mass upon distillation is readily soluble in ether, difficultly soluble in alcohol and tenaciously holds on to the blue pigment. When pure it is snow-white, melts at 53 to 54° and shows all properties of the hydrocarbons of the paraffin series[1]. By extracting the dry flowers with petroleum ether, T. Klobb, J. Garnier and R. Ehrwein[2]) obtained a paraffin melting at 52 to 54° to which they assign the formula $C_{29}H_{60}$. F. B. Power and H. Browning, Jr.[3]) demonstrated the presence of *triacontane,* $C_{30}H_{62}$, m.p. 63 to 65° in chamomile flowers.

The same investigators demonstrated the presence of several other constituents in an oil of chamomile which they obtained

[1]) Report of Schimmel & Co. April 1894, 14.
[2]) Bull. Soc. chim. IV. 7 (1910), 940.
[3]) Journ. Chem. Soc. 105 (1914), 2280.

as a byproduct from the alcoholic extract of chamomile flowers by steam distillation. It remains to be demonstrated whether these substances also occur in the normal oil obtained by direct distillation. Nevertheless, they may be mentioned.

Furfurol was identified by the customary color reactions. Upon standing for some time the oil separated a small amount of a substance that melted at 110°, developed an odor of cumarin when heated, and the solution of which in concentrated sulphuric acid showed a blue fluorescence. This substance is apparently identical with *umbelliferone methyl ether* (herniarin) which melts at 117 to 118° when pure and which had previously been found in *Herniaria hirsuta*, L., family *Caryophyllaceæ*, but not in a volatile oil. Umbelliferone is the lactone of umbellic acid, 2,4-dihydroxycinnamic acid, hence 4-hydroxycumarin. The oil also contained a fatty acid melting at 61°.

$$CH_3 \cdot O \cdot C_6 H_3 \!\!\begin{array}{l} {\diagup} CH\!:\!CH \\ {\diagdown} O \cdot CO \end{array}$$
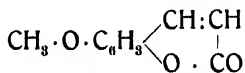
Umbelliferone methyl ether.

Examination. Milfoil oil[1]) is said to be used as an adulterant of chamomile oil for which purpose it is well suited on account of its blue color. The addition of larger amounts, however, are excluded because of the distinctive odor. Moreover, milfoil oil is rather expensive itself. More frequently cedarwood oil[2]) appears to be employed. Its presence can be distinctly recognized when the odor of an oil thus adulterated is compared with that of a genuine one. The addition of cedarwood oil or other oils reduces the congealing capacity of this oil. Genuine oil becomes viscid at $+ 15°$ and at $0°$ becomes butyraceous. Adulterated oils remain limpid at this temperature.

899. Oil of Matricaria discoidea.

Matricaria discoidea, D.C. is a North American composite that has migrated to Europe. It resembles the German chamomile but is smaller. It is further differentiated by the fact that the ray florets are greatly reduced.

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[1]) Chem. Ztg. 8 (1884), 268 and 19 (1895), 358.
[2]) Report of Schimmel & Co. April 1895, 24.

Upon distillation of the entire plant Schimmel & Co.[1]) obtained 0.15 p.c. of a dark brown oil which, at ordinary temperature was full of paraffin crystals. As to odor it occupied a middle position between ordinary and Roman chamomile oil. $d_{30°}0.9175$; A.V. 18.7; E.V. 77.5. On account of its large paraffin content it did not yield a clear solution with even 90 p.c. alcohol. After two recrystallizations from dilute alcohol the paraffin separated from the oil melted at 58 to 61°.

900. Oil of Matricaria Parthenium.

Origin and Properties. *Matricaria Parthenium*, L. *(Pyrethrum Parthenium*, Sm., *Chrysanthemum Parthenium*, Pers., Ger. *Mutterkraut)*, is frequently cultivated in Germany and also occurs wild. Formerly it was official as *Herba Matricariæ*. Upon distillation the fresh flowering plant yields 0.02 to 0.07 p.c. of a yellowish to dark green volatile oil, which occasionally separates crystals at ordinary temperature. d 0.908 to 0.960. According to Chautard the plant that is beginning to produce flower buds yields more oil but is poorer in stearoptene than the flowering plant.

Composition. Matricaria oil is of special interest because in it V. Dessaignes and J. Chautard[2]) first discovered the rare l-*camphor*. In order to obtain this substance the oil is fractionated and the fraction that boils in the neighborhood of 200° is exposed to a freezing mixture. The separated camphor is drained on a force filter.

Plants grown in the neighborhood of Leipzig yielded 0.068 p.c. of oil; $d_{15°}0.960$. At middle temperatures there separated from the oil an abundance of hexagonal crystals which, recrystallized from petroleum ether, melted at 203 to 204° and consisted of l-*borneol*, $[\alpha]_{D} - 36°$. Camphor could not be found in this oil[3]).

The oil examined by Dessaignes and Chautard probably contained borneol as well as camphor. For the oil, after camphor had been frozen out, upon treatment with nitric acid yielded additional camphor. It may be assumed with a fair degree of certainty that the camphor obtained after the treatment with nitric acid owes its origin to borneol.

[2]) Report of Schimmel & Co. October 1911, 107.
[1]) Journ. f. prakt. Chem. 45 (1848), 45.
[3]) Report of Schimmel & Co. October 1894, 68.

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According to Chautard[1]) the oil contains in addition a terpene boiling below 200° which does not yield a solid compound with hydrogen chloride, also a liquid dextrogyrate substance boiling above 200° of higher oxygen content than camphor. In connection with the above-mentioned oil Schimmel & Co. determined a saponification value of 131 thus showing that the oil contains relatively much ester.

901. Oil of Tansy.

Oleum Tanaceti. — Rainfarnöl. — Essence de Tanaisie.

Origin. *Tanacetum vulgare*, L. (*Chrysanthemum Tanacetum,* Karsch) is distributed over most of the European countries and has escaped cultivation in the Atlantic States of North America. It is one of the strongly aromatic composites the volatile oil of the flowers of which has been used as anthelmintic since the Middle Ages.

In North America this plant is cultivated in Michigan (St. Joseph's Co.) and in Indiana. 182 acres were cultivated during 1910, 145 acres during 1911 and 131 acres during 1912. In 1910, 1600 lbs. of oil were produced[2]).

Production. Fresh, flowering tansy yields upon distillation 0.1 to 0.2 p.c., dry material 0.2 to 0.3 p.c. of oil[3]). Most of the commercial oil comes from North America. It is noteworthy that the oils of different origin have somewhat different properties.

Properties. Tansy oil is a yellowish liquid which becomes brown under the influence of air and light.

In connection with the American commercial oils the following constants were determined: $d_{15°}$ 0.925 to 0.935; $\alpha_D + 24$ to $+34°$; $n_{D20°}$ 1.457 to 1.459; A. V. up to 1; E. V. up to 16; E. V. after acetylation 28 (one determination); soluble in 2 to 4 vol. of 70 p.c. alcohol, the diluted solution occasionally shows opales-

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[1]) Journ. de Pharm. III. 44 (1843), 13; Jahresber. d. Chem. 1868, 555.

[2]) Report of Schimmel & Co. October 1910, 132; October 1911, 87; October 1912, 105.

[3]) The yields recorded by O. Leppig (Berl. Berichte 15 [1882], 1088, Referate) namely 1.49 p.c. from the flowers and 0.66 p.c. from the herb cannot pertain to oils obtained by distillation.

cence and even turbidity. The oil distilled from fresh herb has the specific gravity of 0.925 to 0.940; that from dried herb up to 0.955; with 70 p.c. alcohol no clear solution could be obtained.

An oil distilled in Bodenbach, Bohemia, from dried herb with a yield of 0.3 p.c. had the following constants: $d_{15°}$ 0.9398; $\alpha_D + 9°35'$; $n_{D20°}$ 1.47431; soluble in 1.5 vol. of 80 p.c. alcohol with decided separation of paraffin. In connection with a second oil of the same origin the following constants were ascertained: $d_{15°}$ 0.9344; α_D —3°2'; A.V. 1.9; E.V. 33.6; E.V. after acetylation 80.8; soluble in 11 vol. of 70 p.c. alcohol, the solution being turbid, the turbidity, however, disappearing on the further addition of solvent.

An oil[1]) distilled in England from cultivated tansy had but little similarity with the ordinary oil and possessed a decided odor of camphor, similar to that of rosemary. Upon evaporation of the oil a delicate, ambra-like odor finally became perceptible. The camphor content was so large that part of it crystallized out at 0°. The most remarkable difference, however, was its optical rotation for it deviated the ray of polarized light to the left, α_D — 27°.

Composition. The largest part of tansy oil consists of *β-thujone* or tanacetone, a substance to which the oil owes its characteristic odor. It was first isolated in the pure state by G. Bruylants[2]), who regarded it as an aldehyde and named it tanacetylhydride. That it is a ketone and identical with the thujone found by O. Wallach in thuja oil, was demonstrated by F. W. Semmler's[3]) investigations. As shown by the preparation of its semicarbazone Wallach[4]) demonstrated that the thujone of tansy oil consists of the dextrogyrate β-compound. Properties and derivatives of thujone are described in vol. I, p. 461.

Fraction 203 to 205° yielded upon oxidation with chromic acid a small amount of camphor. Bruylants was of the opinion that it contained the alcohol $C_{10}H_{18}O$ corresponding to thujone,

[1]) Report of Schimmel & Co. October 1895, 46.
[2]) Berl. Berichte 11 (1878), 449.
[3]) *Ibidem* 25 (1892), 3343.
[4]) Liebig's Annalen 336 (1904), 267.

and regarded camphor as its oxidation product. Inasmuch, however, as camphor cannot result from thujyl alcohol, it must have resulted from some other constituent or must have been contained in the oil as such. Previously, J. Persoz[1]), also H. Vohl[2]) had obtained camphor after oxidation of the oil with chromic acid. Persoz left it undecided whether camphor was contained in the oil as such or whether it had been formed upon oxidation.

In order to decide this question Schimmel & Co.[3]) fractionated an oil from which thujone had been removed as completely as possible with bisulphite. As the thermometer rose to 205°, a solid, crystalline mass separated in the receiver which was drained by means of force filter and recrystallized from 80 p.c. alcohol. Odor and other properties indicated a mixture of camphor and borneol. For their separation the Haller method[4]) was resorted to which yielded a large amount of camphor and little borneol. The identity of the camphor was proved by the preparation of camphor oxime melting at 116°. The optical rotation showed that it was not the common dextrogyrate variety but the much less common *lævo-camphor*. The angle of rotation of borneol could not be determined because of the small amount of material.

It remains to be ascertained whether thujyl alcohol is present in tansy oil as would seem to be indicated by the statement of Bruylants. In addition the question whether the terpene, b.p. 160°, separated by Bruylants is pinene or camphene should be answered.

According to Peyraud[5]) oil of tansy is exceedingly poisonous and in animals produces a condition related to rabies, *la rage tanacétique,* also known as *simili-rage.* The cause for this may be sought in the poisonous character of thujone[6]).

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[1]) Compt. rend. 13 (1841), 436. — Liebig's Annalen 44 (1842), 313. — Journ. f. prakt. Chem. 25 (1842), 55.

[2]) Arch. der Pharm. 124 (1853), 16; Pharm. Zentralbl. 1858, 318.

[3]) Report of Schimmel & Co. October 1895, 46.

[4]) Compt. rend. 108 (1889), 1308.

[5]) *Ibidem* 105 (1887), 525.

[6]) Comp. F. Jürss, *Beiträge zur Wirkung des Thujons.* Report of Schimmel & Co. October 1903, 126.

902. Oil of Tanacetum boreale.

Half-dried herb of *Tanacetum boreale,* Fisch., a native of Siberia, yielded upon distillation[1]) 0.12 p.c. of an oil with a yellowish color and a strong thujone odor. $d_{15°}$ 0.9218; α_D $+48°25'$; with 8 vol. of 70 p.c. alcohol it yields a turbid solution with copious separation of paraffin.

The oil obtained from fresh herb with a yield of 0.117 p.c.[2]) behaved somewhat differently. It was somewhat more viscid and greenish-brown in color. $d_{15°}$ 0.9603; optical rotation not determinable because of the dark color; $n_{D20°}$ 1.49167; A. V. 30.47; E. V. 40.55; insoluble in 10 vol. of 70 p.c. alcohol, soluble in 2 vol. of 80 p.c. alcohol, the solution becoming turbid upon the addition of more solvent with the separation of *paraffin,* miscible with 90 p.c. alcohol until upon the addition of 0.8 vol. and more turbidity sets in with the separation of paraffin.

903. Oil of Tanacetum Balsamita.

From cultivated, fresh, flowering herb *Tanacetum Balsamita,* L., Ger. *Balsamkraut,* Schimmel & Co.[3]) obtained upon distillation 0.064 p.c. of oil. Its odor was agreeably balsamic, but little characteristic, reminding strongly of tansy: $d_{15°}$ 0.943; α_D $-43°40'$ to $-53°48'$; S. V. 21. In the cold paraffin-like crystals rise to the surface. In 80 p.c. alcohol the oil was insoluble. With 1 to 2 volumes of 90 p.c. alcohol a clear solution resulted which became turbid upon the addition of more solvent, white floccules (paraffin?) separating. Upon distillation the oil passed over between 207 and 283°.

904. Kiku Oil.

In the western part of Japan, kiku oil is distilled in considerable quantity from the leaves and flowers of *Chrysanthemum japonicum,* Thbg. *(Ch. indicum,* L.; *Pyrethrum indicum,* Cass.; Japanese *Kiku).* In 1887 the production amounted to about 1400 kg. It is used as a popular remedy[4]).

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[1]) Report of Schimmel & Co. October 1904, 97.

[2]) *Ibidem* October 1905, 66.

[3]) *Ibidem* October 1897, 60.

[4]) Bericht von Schimmel & Co. April 1888, 46.

Kiku leaf oil is colorless and has a camphor-like odor reminding somewhat of eucalyptus. d 0.885; b. p. 165 to 175°[1]).

Upon distillation of the green leaves G. Perrier[2]) obtained about 0.16 p. c. of volatile oil, the color of which was green and the odor of which reminded of chamomile and peppermint. $d_{15°}$ 0.932; $n_{D18°}$ 1.4931. With 10 parts of 90 p. c. alcohol it gave a clear solution. Cooled to $-15°$ it separated an amorphous, paraffin-like substance. Exposed to a lower temperature it congealed completely. At 160° the oil began to boil. S. V. 8.61. From the saponification liquid hydrochloric acid separated a solid product that had the odor of angelic acid.

Kiku flower oil possesses an odor not at 'all unpleasant. The lower fraction passing over at about 180° has an agreeable odor, the higher fractions smell camphor-like and are not especially agreeable.

905. Riono-Kiku Oil.

From the flowers (?) of *Chrysanthemum sinense* var. *japonicum*, *Riono-Kiku,* S. Keimatsu[3]) obtained 0.8 p. c. of a yellowish-brown oil. It contained i-*camphor*. From 250 g. oil 40 g. were isolated by exposure to low temperature. The camphor was identified by means of its oxime (m. p. 116 to 117°, inactive), paracamphoric acid (*i*-camphoric acid) melting at 202°, and by its β-bromo derivative (m. p. 61°). The oil which remained after the removal of this camphor, but which still contained considerable amounts thereof, had the following properties: $d_{15°}$ 0.9394; $[\alpha]_D$ — 12° 4'; A. V. 0; E. V. 0. In the lower boiling fraction the presence of l-*camphene* was demonstrated by its conversion into *iso*borneol.

906. Oil of Chrysanthemum cinerariæfolium.

The distillation of 24.6 kg. of Dalmatian pyrethrum blossoms (insect powder) yielded Schlagdenhauffen and Reeb[4]) 3 g. of a butyraceous volatile oil. A much larger yield, namely 0.39 p. c.,

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[1]) Bericht von Schimmel & Co. April 1887, 37.

[2]) Bull. Soc. chim. III. 23 (1900), 216.

[3]) Journ. pharm. Soc. of Japan 1909, No. 326, 1.

[4]) Journ. de Pharm. d'Alsace-Lorraine August 1891; Jahresb. f. Pharm. 1891, 61. — Comp. also H. Thoms, *ibidem*.

was obtained by H. Haensel[1]) upon distillation of the flowers of
Chrysanthemum cinerariæfolium (Trev.), Bocc., which yield the
Dalmatian insect powder. The oil was a brown liquid of agreeable
odor that began to congeal at 28° and was solid at ordinary
temperature.

P. Siedler[2]) distilled 30 kg. of prime quality, half-open Dalmatian
blossoms of the latest harvest and obtained 20.212 g. = 0.067 p.c.
(by shaking the aqueous distillate with ether) of a salve-like mass
of strongly aromatic odor. Of solid constituents it contained
a *paraffin* $C_{11}H_{80}$ melting at 54 to 56°, also a substance melting
at 62°, presumably *palmitic acid*. The liquid portion of the oil
contained a *phenol* and *an acid* that had the odor of butyric
acid, but was not farther characterized. It may be regarded as
demonstrated that the insecticide principle is not contained
among the constituents volatile with water vapor.

907. Estragon Oil.

Oleum Dracunculi. — Esdragonöl. — Essence d'Estragon.

Origin. Estragon oil which is used in conserves and in the
preparation of aromatic vinegars, is distilled from the flowering
herb of *Artemesia Dracunculus*, L. Dry herb yields 0.25 to 0.8 p.c.,
fresh herb 0.1 to 0.4 p.c.

Properties. Estragon oil is a colorless to yellowish-green
liquid of a peculiar anise-like odor and a strongly aromatic, but
not sweet taste. $d_{15°}$ 0.900 to 0.945; α_D + 2 to + 9°; $n_{D20°}$ 1.502
to 1.514; A. V. up to 1; E. V. 1 to 9; E. V. after acetylation 15
(one determination); soluble in 6 to 11 vol. and more of 80 p.c.
alcohol, also in 1 vol. and more of 90 p.c. alcohol.

An oil distilled by Roure-Bertrand Fils[3]) revealed rather
different properties, namely the following: $d_{15°}$ 0.9814; α_D + 2°56′;
S. V. 29.8.

The oil should be stored in well-stoppered, completely filled
bottles otherwise the methyl chavicol is oxidized to an aldehyde
which increases the specific gravity, the index of refraction and

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[1]) Pharm. Ztg. 43 (1898), 760.

[2]) Berichte d. deutsch. pharm. Ges. 25 (1915), 297.

[3]) Berichte von Roure-Bertrand Fils October 1910, 43.

the solubility in 80 p.c. alcohol. An oil with the following properties: $d_{15°}$ 0.9168; $\alpha_D + 3°10'$; $n_{D20°}$ 1.50847; soluble in 1 vol. and more of 90 p.c. alcohol; after standing for six months in an open bottle had the following properties: $d_{15°}$ 1.0475; $\alpha_D + 3°10'$; $n_{D20°}$ 1.52493; soluble in 1 vol. and more of 80 p.c. alcohol. It reacted when shaken with bisulphite solution.

Composition. Estragon oil was first investigated by Laurent[1]). Upon oxidation he obtained an acid melting at 175° which he designated dragonic acid. C. Gerhardt[2]) recognized this acid as anisic acid. Inasmuch as this oil behaved like anise oil toward sulphuric acid and other reagents, he declared both oils as identical. Since that time anethol has been regarded as the principal constituent of estragon oil. When in 1892 methyl chavicol (p-methoxy allyl phenol), an isomer of anethol, (p-methoxy propenyl phenol) was shown for the first time in the laboratory of Schimmel & Co. to be a constituent of a volatile oil, namely, anise bark oil, its estragon-like odor attracted attention. An investigation undertaken in consequence of this observation, showed that estragon consists for the most part of *methyl chavicol,* but contains no anethol[3]).

Upon energetic oxidation, methyl chavicol (see vol. I, p. 475) like anethol, yields anisic acid; gentle oxidation with potassium permanganate, however, yields *homo*anisic acid. The statement made by Gerhardt that the acid obtained by oxidation of estragon oil is anisic acid was, therefore, correct. However, the conclusion that the oil contains anethol was wrong.

Later methyl chavicol was also found in estragon oil by E. Grimaux[4]) and designated "estragol" although there was no excuse for re-naming a known substance the presence of which in this oil had previously been established.

Additional constituents are reported on by Daufresne[5]) who examined German as well as French oils.

[1]) Liebig's Annalen 44 (1842), 313.
[2]) Compt. rend. 19 (1844), 489. — Liebig's Annalen 52 (1844), 401.
[3]) Report of Schimmel & Co. April 1892, 30.
[4]) Compt. rend. 117 (1893), 1089.
[5]) *Etude de l'essence d'estragon et de quelques dérivés de l'estragol.* *Thèse,* Paris 1907. — Compt. rend. 145 (1907), 875. — Bull. Soc. chim. IV. 3 (1908), 330.

Fraction 173 to 175° (760 mm.) had the following constants: $d_{15°}$ 0.812; α_{D} +29°44'; $n_{D15°}$ 1.48636; mol. refr. found 48.04, which indicates an aliphatic hydrocarbon with three double bonds similar to *ocimene* but not identical therewith. Upon reduction dihydromyrcene resulted: b.p. 66° (12 mm.); $d_{15°}$ 0.7972; $n_{D15°}$ 1.45782; mol. refr. found 47.19. According to the method of Bertram-Walbaum the hydrocarbon yielded a product that boiled at 95 to 100° (15 mm.) and had the odor of linalyl acetate.

The terpene fraction which contributed 15 to 20 p.c. of the oil contained in addition a hydrocarbon which possibly is identical with *phellandrene*.

Furthermore Daufresne found in a 16 year old German oil *p-methoxycinnamic aldehyde* (b.p. 170° under 14 mm. pressure; $d_{0°}$ 1.137; m.p. of semicarbazone 222°; m.p. of oxime 154°). This oil contained 4.5 p.c., whereas a French oil contained but 0.5 p.c., and another German oil 0.4 p.c. The bisulphite addition product was difficultly decomposable. Oxidation with permanganate in acid solution yielded anisic acid (m.p. 184°), whereas oxidation with silver oxide yielded *p*-methoxycinnamic acid (m.p. 170°). Comparison with synthetic *p*-methoxycinnamic aldehyde, prepared according to M. Scholtz and A. Wiedemann[1]), established the identity of the two substances. The higher boiling fractions of the oil split off water and resinified. They were lævogyrate and possibly contained an *aldol*[2]).

908. Oil of Levant Wormseed.

Origin and Production. Levant wormseed, *Semen Cinæ,* Ger. *Wurmsamen* or *Zitwersamen*, which contains santonin, is used in popular medicine as anthelmintic. It consists of the unexpanded floral blossom of *Artemesia maritima,* L. var. *Stechmanni (A. Cina,* Berg). This plant occurs only in Russian Turkestan[3]). The area on the left bank of the Syr-Darja is rather limited, whereas that on the right bank is more extended. It covers the shores and valleys of the larger and smaller rivers as far as the Altai. The

[1]) Berl. Berichte **36** (1903), 853.

[2]) Comp. also Daufresne and Flament, Bull. Soc. chim. IV. **3** (1908), 656.

[3]) Westnik finanzov **1912,** Nr. 33; Pharm. Ztg. **57** (1912), 778; Chem. Ztg. **37** (1913), 620.

monopoly to collect is farmed out by the Government. The largest
santonin content is found in the blossoms that have just ex-
panded. Inasmuch as the unfolding takes place very rapidly, the
harvest, which usually takes place toward the end of August,
must be accomplished within two weeks.

As is the case with all other wild plants in treeless prairies,
a large part of the *Artemisia* is collected annually as fuel. That
the plant has not been completely exterminated is due first to the
circumstance that it is perennial and secondly to the fact that some
of it has matured sufficiently when harvested to sow itself. Many
plants are also destroyed by the herds of sheep grazing in those
regions. Rational culture would yield per desjatine (= abt. $2^3/4$ acres)
150000 to 300000 poods (= 2450000 to 4900000 kg.) of *Flores Cinæ*.

The largest part of Levant wormseed, about nine-tenths, is
used for the manufacture of santonin, in the production of which
the oil was formerly obtained as a byproduct. Inasmuch as the
santonin factories have for some time abandoned the production
of the oil, the price of the latter rose so as to reduce its con-
sumption materially. The fact that cineol, or eucalyptol, the
principal constituent of Levant wormseed oil, can be had at a
very low price, may have had something to do with it.

The yield obtained upon distillation amounts to 2 to 3 p.c.

Properties. Oil of Levant wormseed is a yellow liquid having
the camphor-like odor of cineol, which is accompanied by an
unpleasant odor peculiar to the "seed". $d_{15°}$ 0.915 to 0.940;
α_D — 1° 50' to — 7°; $n_{D20°}$ 1.465 to 1.469; soluble in 2 to 3 vol.
and more of 70 p.c. alcohol.

Composition. Although Levant wormseed oil had been inves-
tigated repeatedly, the results were not satisfactory so far as the
principal constituents are concerned, since they contradicted each
other in points not inessential. The views concerning the hydro-
carbons resulting from the dehydration of the substance $C_{10}H_{18}O$
were especially divergent. Whereas C. Völckel[1]), H. Hirzel[2]),
K. Kraut and Wahlforss[3]), also C. Gräbe[4]) claimed that the

[1]) Liebig's Annalen 38 (1841), 110; 87 (1853), 312; 89 (1854), 358.
[2]) Jahresber. d. Chem. 1854, 591 and 1855, 655.
[3]) Liebig's Annalen 128 (1864), 293.
[4]) Berl. Berichte 5 (1872), 680.

action of phosphoric acid anhydride yielded a hydrocarbon $C_{10}H_{16}$. C. Faust and J. Homeyer[1]) proved that the hydrocarbon, known as "cynene" is identical with cymene.

All of these contradictory statements were cleared up by two almost simultaneous contributions, the one by O. Wallach and W. Brass[2]), the other by C. Hell and H. Stürcke[3]).

Wallach and Brass first isolated in a pure condition the oxygenated constituent, of which the bulk of Levant wormseed oil is composed. By passing hydrogen chloride into the oil they obtained a crystalline addition product which was decomposed with water. This oxygenated constituent they named *cineol* and showed that hydrogen chloride and benzoyl chloride will dehydrate it with the formation of a terpene, cynene, later designated *dipentene*. In addition they showed that, under the influence of concentrated sulphuric acid or phosphoric acid, dipentene yields cymene. Thus were explained the deviating results of earlier chemists. According to the strength of dehydrating agent and the conditions under which it was employed, they had obtained mixtures of both hydrocarbons in which either dipentene or cymene predominated.

Later J. Schindelmeiser[4]) showed the presence of i-*α-pinene* in the lowest boiling fraction (m.p. of nitrosochloride 103 to 104°; m.p. of hydrochloride 123°), that of *terpinene* (m.p. of nitrosite 155 to 157°) in the middle fraction, also that of l-*α-terpineol* (m.p. of nitrosochloride 103"; terpin hydrate; m.p. of dipentene dihydrochloride 48°).

These results were verified by Schimmel & Co.[5]). In addition to *α*-terpineol they found a *terpinenol* (b.p. 208 to 218°) in the alcohol fraction. With hydrochloric acid they obtained terpinene dihydrochloride (m. p. 52°) and with 3 p.c. sulphuric acid *cis*-terpin hydrate (m. p. 116 to 117°). Whether the alcohol was *α*- or *β*-terpinenol could not be decided.

The higher boiling fractions (b. p. 230 to 260°) contain a *sesquiterpene* (d_{15}. 0.9170). A solid nitrosochloride was not obtained,

[1]) Berl. Berichte 7 (1874), 1429.
[2]) Liebig's Annalen 225 (1884), 291.
[3]) Berl. Berichte 17 (1884), 1970.
[4]) Apotheker Ztg. 22 (1907), 876.
[5]) Report of Schimmel & Co. November 1908, 143.

neither a hydrochloride nor a bromide. From the distillation residue of the oil (b. p. above 280°) crystals separated slowly. These may be a solid sesquiterpene alcohol[1]) or the paraffin $C_{32}H_{66}$ (m. p. 55 to 58°) which T. Klobb, J. Garnier and R. Ehrwein[2]) found in the flowers of this plant.

909. Oil of Doz.

From Bombay Schimmel & Co.[3]) obtained an herb named *Doz* which, according to its botanical examination, may be a variety of *Artemisia maritima,* L. However, nothing definite could be ascertained for not a single flower was present. A trial distillation yielded 0.24 p.c. of a dark green oil of a peculiar but not distinctive odor. $d_{15°}$ 0.9696; A. V. 1.8; E. V. 4.2; soluble in about 3 vol. of 70 p.c. alcohol with the separation of paraffin. On account of its dark color the optical rotation of the oil could not be ascertained. The few grams of oil precluded a detailed examination.

910. Oil of Wormwood.
Oleum Absinthii. — Wermutöl. — Essence d'Absinthe.

Origin. *Artemisia Absinthium,* L., is indigenous in many countries of the old world as far north as Scandinavia, Finland and Siberia, and has migrated to North America. For commercial purposes the plant is frequently cultivated.

Previous to the prohibition of absinthe in France the small or Roman wormwood, *Artemisia pontica,* L. was cultivated as well as the common or large wormwood. In addition the wild ordinary plant was used for the distillation of the oil.

Production. Since the production and the sale of oil and of the beverage absinthe have been prohibited in France[4]), the cultivation of wormwood which was formerly extense, and the distillation of oil connected therewith, has ceased almost entirely[5]). Hence the cultivation in North America has taken

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[1]) Report of Schimmel & Co. November 1908, 143.

[2]) Bull. Soc. chim. IV. 7 (1910), 940.

[3]) Report of Schimmel & Co. April 1915, 51.

[4]) Comp. Berichte von Roure-Bertrand Fils April 1907, 43.

[5]) Report of Schimmel & Co. November 1908, 127. — Berichte von Roure-Bertrand Fils October 1912, 82; October 1913, 56; April 1914, 44.

first place. During 1911 about 404 acres were under cultivation
in Michigan and Indiana yielding about 8000 lbs. of oil. Wayne Co.,
N.Y., had about 21 acres under cultivation with an estimated
yield of 370 lbs. of oil[1]). The area cultivated in Sauk Co., Wis.,
also appears to be fairly large[2]). The importance of the worm-
wood cultivation in this state lies in the rotation of crops;
wormwood, Indian corn, oats or barley. A very good oil is
produced in Miltitz near Leipzig by Schimmel & Co. from home-
grown plants. Algeria, Italy and Spain also supply wormwood
oils though not in considerable amounts.

Concerning the yield and character of the oil it should
be pointed out that they vary considerably according to the
condition of the herb (fresh, moist, half dry, dry) and the length
of distillation. If the still is charged with fresh herb during
wet weather, the yield may be but half of the normal. Indeed,
wet herb can scarcely be exhausted for the oil is but slowly
extracted from the pasty mass, so that the complete exhaustion
would not pay for the steam. Under favorable conditions fresh
herb may yield 0.5 p.c. of oil.

In France wormwood is frequently distilled together with
lavender flowers or with the herb of *Calamintha Nepeta,* L.
The reason given is to obtain a more limpid oil.

Concerning the formation and distribution of the volatile oil
in wormwood, investigations have been made by E. Charabot[3])
and G. Laloue[4]).

Properties. Oil of wormwood is occasionally a somewhat
viscid liquid. The color is either dark green, occasionally blue,
or brown. The odor is the unpleasant odor of the plant. The
taste is bitter, scratching and persistent.

For reasons enumerated in a previous paragraph, the
properties of individual oils vary so greatly that it is frequently
impossible to draw conclusions as to the source or purity of

[1]) Report of Schimmel & Co. October 1911, 100.
[2]) R. H. Denniston and R. E. Kremers, Bull. Univ. Wisconsin, Serial
No. 738, Gen. Ser. No. 542. Madison 1914, p. 32; Report of Schimmel & Co.
October 1915, 43.
[3]) Compt. rend. 130 (1900), 923. — Bull. Soc. chim. III. 23 (1900), 474.
[4]) Berichte von Roure-Bertrand Fils April 1906, 3. — Compt. rend. 144
(1907), 152. — Bull. Soc. chim. IV. 1 (1907), 280, 640.

commercial oils. On account of the dark color, the optical rotation of the oil is not directly determinable. Using a 1 p.c. alcoholic solution in a 20 mm. tube the dextrorotation of a series of commercial oils was determined. Computed for the oil itself they corresponded to $\alpha_D + 40$ to $+70°$. The oil distilled in Barrême from wild plants (p. 641) showed a lævorotation of -- $16°40'$ when determined in this manner.

The constants determined in connection with a large number of wormwood oils are herewith tabulated: —

Commercial Oils.

	French	Algerian .	Italian	American
$d_{15°}$	0.901 to 0.954 (mostly above 0.92)	0.905 to 0.939	0.918 to 0.943	0.916 to 0.938
$n_{D20°}$	1.46684 (1 determination)	—	—	—
A.V.	up to 6.7	up to 6.1	up to 5.6	up to 2.2
E.V.	11 to 108 (in one instance 135)	14 to 93	15 to 37	46 to 89
E.V. after acetyl.	—	—	123.2	113.9
Solubility in 80 p.c. alcohol	Soluble in 1 to 2 vol. Additional solvent occasionally causes turbidity. At times the oil is not completely soluble.			Soluble in 1 to 2 vol. More solvent occasionally causes opalescence.
Solubility in 90 p.c. alcohol	Readily soluble. Solution is clear from the beginning or up on the addition of 0.5 to 1 vol. Only in isolated cases does dilution cause turbidity.			Soluble in all proportions.

Distillates of Schimmel & Co.

a) Distilled in *Miltitz:*

Variety of herb:	Hungarian		Miltitz	French, cultivated in Miltitz
$d_{15°}$ . . . . : . .	0.8845	0.9125	0.932 to 0.954	0.9276 to 0.9331
A.V.	—	16.8	0.2 to 8.6	up to 1.5
E.V..	35.0	75.4	76 to 185	38.8 to 65.3
E.V. after acetyl.	—	—	153 to 222	93.3 to 170.3
Solubility and boiling temperature	Insoluble in 80 p.c. alcohol. Readily soluble in 90 p.c. alcohol.	Insoluble in 80 p.c. alcohol. Soluble in 95 p.c. alcohol. Sol. at first clear, later turbid.	Mostly soluble even in 80 p.c. alcohol (1 to 4 vol.); sol. in all proportions of 90 p.c. alcohol, occasionally 0.5 to 1 vol. are required. The bulk boils between 36 and 90° under 4 mm. pressure. All fractions strongly dextrogyrate, $+55$ to $+75°$.	Sol. in 1 to 1.5 vol. of 80 p.c. alcohol. In one instance additional solvent caused turbidity. Soluble in all proportions of 90 p.c. alcohol.

b) Distilled in *Barrême:*

Variety of herb	Wild herb	Cultivated herb
$d_{15°}$	0.901 to 0 908	0.936 to 0.939
A.V..	up to 3.2	up to 2.8
E.V..	34.3 to 57.4	96.4 to 114
E.V. after acetyl.	—	164.5
Solubility . . .	Even with 90 p.c. alcohol its solutions are clear only at first.	Does not yield a clear solution with 80 p.c. alcohol. With 90 p.c. alcohol one of the oils yielded a clear solution, the other two oils yielded solutions which were clear only when concentrated.
Boiling temperature	Under 3 mm. press. it boiled for the most part betw. 40 and 100°. All fractions were lævogyrate, from — 3° 26' to — 21° 10' (*l*-thujone?).	Under 4 mm. pressure, a large part of the oil comes over between 45 and 97°. All fractions strongly dextrogyrate from + 51° 28' to + 72° 20'. The presence of pinene could not be proven with certainty.

An oil distilled from wild Dalmatian herb had the following properties[1]): $d_{15°}$ 0.9188; A.V. 1.3; E.V. 64.6; soluble in 1 vol. and more of 80 p.c. alcohol.

According to E. Charabot[2]) the relation of thujone to thujyl alcohol changes with the degree of development of the plant, the thujone, which is present originally, disappearing and being converted in part to thujyl alcohol. Oils distilled from plants at different times show the following differences: —

	$d_{24°}$	Ester content	Thujyl alcohol			Thujone
			combined	free	total	
No. 1 . .	0.9307	9.7 p.c.	7.6 p.c.	9.0 p.c.	16.6 p.c.	43.1 p.c.
„ 2 . .	0.9253	13.1 p.c.	10.3 p.c.	9.2 p.c.	19.5 p.c.	35.0 p.c.

Roure-Bertrand Fils[3]) distilled two oils of wild wormwood which had grown in the hills about Caussols (Maritime Alps). One was distilled in 1900, the other in 1905. Their analysis yielded the following results: —

	1900	1905
Ester	9.0 p.c.	5.5 p.c.
Combined alcohol .	7.0 p.c.	4.3 p.c.
Free alcohol . . .	71.9 p.c.	76.3 p.c.
Thujone	8.4 p.c.	3.0 p.c.

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[1]) Report of Schimmel & Co. October 1911, 101.
[2]) Compt. rend. 130 (1900), 923. — Bull. Soc. chim. III. 23 (1900), 474.
[3]) Berichte von Roure-Bertrand Fils April 1906, 36.

These oils contained only a small amount of thujone, thujyl-alcohol being the principal constituent. An oil distilled by the same firm from plants cultivated in Grasse had the following properties: ester 35.6 p.c.; alcohol ester 27.9 p.c.; free alcohol 12.3 p.c.; thujone 7.6 p.c. As will be seen thujylalcohol was also the principal constituent of this oil, but more of it was combined than in the oil from the wild plants.

Composition. The first chemical investigation of wormwood oil was made by F. Leblanc[1]). After several rectifications of the oil over lime he obtained a distillate at 205° which was the principal constituent of the oil and the composition of which he correctly determined as $C_{10}H_{16}O$. Treatment with phosphoric acid anhydride yielded a hydrocarbon $C_{10}H_{14}$. These results were later verified by a A. Cahours[2]), H. Schwanert[3]), and J. H. Gladstone[4]). F. Beilstein and A. Kupffer[5]) named the substance $C_{10}H_{16}O$ *absynthol* and ascertained that dehydration yields cymene. They also verified Gladstone's statement that the constituent which distills over between 270 and 300° is identical with the corresponding fraction from chamomile oil.

Upon shaking the individual fractions with potassa solution, Beilstein and Kupffer isolated an acid the analysis of the barium salt of which identified it as *acetic acid*.

Semmler[6]) first pointed out the identity of absynthol with *tanacetone* or *thujone*. For the properties of thujone see vol. I, p. 461.

The results of the investigation of the other constituents made in their New York laboratory are reported by Schimmel & Co.[7]). The oil distilled by themselves was first deprived of its thujone as completely as possible by treatment with sodium

[1]) Compt. rend. **21** (1845), 379. — Annal. de Chim. et Phys. III. **16** (1846), 333; Chem. Zentralbl. **1846**, 62.

[2]) Compt. rend. **25** (1847), 725.

[3]) Liebig's Annalen **128** (1863), 110.

[4]) Journ. Chem. Soc. **17** (1864), 1 *et seq.*; Jahresber. d. Chem. **1868**, 549.

[5]) Liebig's Annalen **170** (1873), 290.

[6]) Berl. Berichte **25** (1892), 3350. Comp. also *ibidem* **27** (1894), 895. furthermore Report of Schimmel & Co. October **1894**, 56 and Wallach, Liebig's Annalen **286** (1895), 93.

[7]) Report of Schimmel & Co. April **1897**, 47.

bisulphite solution with the addition of alcohol. The remaining oil was saponified with alcoholic sodium hydroxide. After recovery of the alcohol, the saponified oil was distilled with steam. A considerable viscid residue was obtained that was only partly soluble in ether. The ether insoluble portion revealed itself as the sodium salt of an acid which was recognized as *palmitic acid* by the determination of its melting point and analysis of its silver salt. The aqueous saponification liquid was neutralized with sulphuric acid and evaporated to dryness and the residue extracted with absolute alcohol. The acids of the organic sodium salts extracted by alcohol were esterified and the esters separated by fractional distillation. As is the case with the esters of most volatile oils this acid mixture consisted of *acetic* and iso*valeric acids*.

The steam-distilled oil was first fractionated several times under diminished pressure, after which the lower fractions were refractionated under ordinary pressure. Thus a very small fraction 158 to 168° was obtained in which the presence of *phellandrene* was proven. An attempt to identify pinene by means of its nitrosochloride resulted in the characteristic blue coloration. A few crystals were also obtained but the amount was too small to make possible the identification of pinene[1]).

Fraction 200 to 203° revealed itself as thujone which cannot be removed completely from the original oil by treatment with bisulphite. It was readily characterized by its bisulphite compound, also by its tribromide melting at 121 to 122°. From fraction 210 to 215° these two derivatives could not be obtained. This fraction was alcoholic in nature as shown by acetylation and subsequent saponification. Careful oxidation with chromic acid mixture converted it almost quantitatively into thujone, thus proving the presence of *thujyl* (tanacetyl) *alcohol*.

In a still higher fraction, 260 to 280°, which was obtained in relatively large amount, the presence of *cadinene* was demonstrated by the formation of its hydrochloride melting at 117 to 118°.

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[1]) C. R. A. Wright (Pharmaceutical Journ. III. 5 [1874], 233) found two hydrocarbons in the oil, one of which boiled at 150°, the other between 170 to 180°. J. W. Brühl (Berl. Berichte 21 [1888], 156) is of the opinion that the physical properties of the terpene boiling around 160° and mentioned by Gladstone indicate *d*-pinene.

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Finally, the amount of thujylalcohol and *thujylacetate* in the original oil was ascertained by quantitative saponification of the original as well as the acetylated oil: 17.6 p.c. of thujylacetate (corresponding to 13.9 p.c. thujyl alcohol) and a total of 24.2 p.c. of thujylalcohol (free and as ester) were ascertained.

According to this investigation wormwood oil is composed of 1. *thujone*, $C_{10}H_{16}O$; 2. *thujylalcohol*, $C_{10}H_{18}O$, free as well as ester of *acetic,* iso*valeric* and *palmitic acids;* 3. *phellandrene* and possibly *pinene;* 4. *cadinene;* 5. a *blue fraction* the composition of which has not been definitely determined.

According to O. Wallach[1]) the thujone of wormwood oil is for the most part dextrorotatory *β-thujone* as revealed by the melting point of the semicarbazone characteristic of this form. In addition there is present a small amount of a second thujone, for upon crystallization of the crude semicarbazones low melting fractions with much lower optical rotation were obtained.

In a Spanish wormwood oil F. Elze[2]) found *nerol.*

In an Italian oil V. Paolini and R. Lomonaco[3]) found besides *α-* and *β-*thujone, an isomeric thujylalcohol which they designate *ð-thujylalcohol.* It is the same which Paolini and B. Divizia[4]) had previously obtained among the reduction products of French wormwood oil.

Since the oil of wild wormwood is lævogyrate, it possibly contains *α-thujone.* Comp. under Properties p. 641.

Whether formic and salicylic acids, which were found by R. C. Roark[5]) in the saponification liquid of a Wisconsin oil, are normal constituents cannot be determined until their presence has been shown in oils of undoubted purity.

Examination. Turpentine oil is the principal adulterant. However, since wormwood oil contains but little terpene, its presence is readily detectable. The first 10 p.c. distilled from

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[1]) Liebig's Annalen 336 (1904), 268.

[2]) Chem. Ztg. 34 (1910), 857.

[3]) Atti R. Accad. dei Lincei, Rome (5) 23 (1914), II. 123; Chem. Zentralbl. 1915, I. 607.

[4]) Atti R. Accad. dei Lincei, Rome (5) 21 (1912), I. 570; Chem. Zentralbl. 1912, II. 256.

[5]) Midl. Drugg. and pharm. Review 45 (1911), 237; Report of Schimmel & Co. October 1911, 101.

oil of wormwood should yield a clear solution with 2 parts of 80 p.c. alcohol.

In this manner L. F. Kebler[1]) detected turpentine oil in four out of eight samples, apparently of American origin. In some of the samples its presence could be detected by the odor.

911. Oil of Artemisia arborescens.

From the dry herb of *Artemisia arborescens*, L., which shrub-like plant is common in the Mediterranean countries, Schimmel & Co.[2]) obtained 0.62 p.c. of a deep blue oil with an odor equal to that of French wormwood oil. $d_{15°}$ 0.9458; A.V. 9.8; E.V. 19.5; soluble in about 10 vol. of 80 p.c. alcohol.

T. Jona[3]) found 13.94 p.c. alcohols $C_{10}H_{18}O$, free and as ester, of which *borneol* (m.p. 203 to 205°; b.p. 212°) and *thujyl alcohol* (b.p. 211 to 212"; oxidation to thujone) were identified. In addition the oil contained 13 p.c. *β-thujone*, $[\alpha]_{D21°}$ + 76.02°, which boiled at 200 to 202° and yielded a tribromide melting at 122°. The saponification liquid contained a mixture of fatty acids, presumably *formic, acetic,* iso*valeric, pelargonic, palmitic* and *stearic acids.*

912. Oil of Artemisia vulgaris.

GERMAN "BEIFUSSÖL".

Artemisia vulgaris, L., which is a common weed along hedges and roadsides, contains volatile oil in all its parts. From the *root 0.1 p.c., from the herb 0.026[4]) to 0.2 p.c. were obtained.

The root oil is greenish-yellow, butyraceous, crystalline[5]). It has a disagreeable bitter taste, burning at first, then cooling.

. The odor of the oil from the herb is but little characteristic. $d_{15°}$ 0.907. According to an observation made in the laboratory of Schimmel & Co. it contains *cineol.*

For herb oil H. Haensel[4]) found $d_{20°}$ 0.9279. The addition of 90 p.c. alcohol caused the separation of colorless laminæ (paraffin?). Ammoniacal silver solution produced a decided aldehyde reaction.

[1]) Americ. Journ. Pharm. 74 (1902), 142.

[2]) Report of Schimmel & Co. November 1908, 136.

[3]) Ann. Chimica appl. 1 (1914), II. 63.

[4]) Chem. Zentralbl. 1908, II. 1436.

[5]) Bretz and Elieson, Taschenbuch für Chemiker und Apotheker 1826, 61.

JAPANESE YOMUGI OIL.

Schimmel & Co.[1]) have examined two samples of Japanese yomugi oil[2]): $d_{15°}$ 0.9101 and 0.9126; α_D — 13° 16′ and — 18° 50′; $n_{D20°}$ 1.47763 and 1.48547; A. V. 1.56 and 1.32; E. V. 29.81 and 16.19; with 90 p. c. alcohol it does not yield a clear solution. The oil contains *cineol* (iodol derivative) and probably *thujone*.

CHINESE NGAI YAU OIL.

An oil that was sent from Hongkong to the Imperial Institute in London under the name of Ngai Yau was probably derived from *Artemisia vulgaris*, L., $d_{15°}$ 0.9390; S. V. 103.3; S. V. after acetylation 205.87[3]).

This Chinese oil is used principally in medicine. Internally it is administered by adding it in drop doses to tea for colds and like affections, externally it is applied as liniment in rheumatism and similar diseases. The Chinese sell the oil in small bottles as a patent medicine. The wholesale price was $ 400.— per picul, that is about $ 1.45 in gold per pound[4]).

INDIAN WORMWOOD OIL.

The Indian Museum in Calcutta sent an oil labled "Indian wormwood oil" to Schimmel & Co. which had been distilled in Lebong, Darjeeling district (Bengal) from the herb (*Artemisia vulgaris*, L., *A. indica*, Willd.). It had a yellow color with a greenish fluorescence and its odor reminded of sage. $d_{15°}$ 0.9219; α_D — 8° 52′; $n_{D20°}$ 1.46201; A. V. 1.2; E. V. 22.1; E. V. after acetylation 55.5; soluble in 1 vol. of 80 p. c. alcohol, the addition of more than 5 volumes causing opalescence and, upon standing, the separation of crystals of paraffin. With the aid of semicarbazide *α-thujone* could be separated from the oil, the semicarbazide melting at 186°, its $[\alpha]_D$ + 64.4° (in alcoholic solution). The thujone regenerated from the semicarbazone with phthalic acid anhydride was, strange to note, optically inactive. The

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[1]) Report of Schimmel & Co. October 1903, 78; April 1904, 78.

[2]) According to J. J. Rein (*Japan, nach Reisen und Studien*, Leipzig 1886, II. p. 160) *"Yomogi"* is the Japanese designation for *Artemisia vulgaris*.

[3]) Bull. Imp. Inst. 11 (1913), 436.

[4]) Daily Cons. and Trade Rep., Washington 17 (1914), No. 56, p. 906.

[5]) Report of Schimmel & Co. April 1918, 28.

odor of the oil renders the presence of borneol probable, however, the amount of material was insufficient to establish its presence.

An oil sent to the Botanical Institute in Buitenzorg which had been distilled from plants growing wild in the Tengger mountains, eastern Java, is supposed to have been obtained from *Artemisia indica* (without author)[1]. Although the optical rotation was opposite to that of the oil described above, it must be assumed that the oil was distilled from *A. indica*, Willd. $=$ *A. vulgaris*, L. $d_{26°}$ 0.949; $\alpha_{D26°}$ 57° 2'; S. V. 99; E. V. after acetylation 228. The yield from dry leaves was 0.28 p.c. of oil. From the acetylation value a thujyl alcohol content of 62.7 p.c. was erroneously computed, whereas it corresponds to one of 75.6 p.c. Upon distillation about 18 p.c. went over between 170 and 190°, about 19 p.c. between 190 and 215° and about 52 p.c. between 215 and 300°, the residue amounting to about 11 p.c. The presence of thujone could not be established.

Schimmel & Co.[2]) have described two oils from the same source and of like origin.

1. Oil from younger plants: golden-yellow; $d_{15°}$ 0.9573; α_D + 55° 54'; A.V. 6.7; E.V. 121.6; soluble in 1 vol. and more of 80 p.c. alcohol, opalescence resulting from the addition of 10 vol. of solvent.

2. Oil from old plants: brownish-yellow; $d_{15°}$ 0.9595; α_D + 38° 40'; A.V. 5.0; E.V. 138.7; soluble in 1 vol. of 80 p.c. alcohol, the addition of more than 2 vol. of solvent causing turbidity. Attempts to acetylate the oils were without result, for when the oil was boiled with acetic acid anhydride it was partially decomposed.

913. Oil of Artemisia gallica.

According to E. Heckel and F. Schlagdenhauffen[3]), *Artemisia gallica*, Willd., which is widely distributed in France, contains, in addition to santonin, about 1 p.c. of volatile oil, in the production of which small amounts of a crystalline substance (camphor?) is simultaneously obtained. As to the properties of the oil nothing is known.

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[1]) Jaarb. dep. Landb. in Ned.-Indië 1906, 44. Batavia 1907.

[2]) Report of Schimmel & Co. November 1908, 140.

[3]) Compt. rend. 100 (1885), 804.

914. Oil of Artemisia Barrelieri.

The oil distilled from the flowering plant of *Artemisia Barrelieri,* Bess. finds medicinal application in Spain in colics and hysterical and epileptic attacks. It is also said to be used in the manufacture of Algerian absinth.

The odor is agreeable, strongly aromatic and reminds much of tansy[1]). $d_{15°}$ 0.923. It boils between 180 and 210° and consists almost entirely of *thujone*[2]), a fact that explains its similarity with wormwood and tansy oils. The oil would be suited very much for the production of pure thujone provided it could be had in larger amounts.

As shown by O. Wallach[3]), the thujone was a mixture of the α- and β-varieties.

915. Oil of Artemisia glacialis.

The dried herb of *Artemisia glacialis,* L., Ger. *Alpenbeifuss,* known in commerce as *Génépi des Alpes*[4]), Ger. *Genepikraut,* yields upon distillation 0.15 to 0.3 p.c. of volatile oil of strongly aromatic odor. $d_{20°}$ 0.964. It boils between 195 and 310". Inasmuch as it contains a fatty acid that melts at 16°, the oil congeals at 0° to a butyraceous mass[5]).

916. Oil of Artemisia Herba-alba.

From the fresh non-flowering herb of *Artemisia Herba-alba,* Asso, a plant that is widely distributed in Algeria and is used as a favorite remedy, E. Grimal[6]) obtained, by means of water distillation, a greenish-yellow oil of exceedingly pleasant odor. 150 kg. of herb yielded 450 g. of oil, hence about 0.3 p.c. The oil examined by him in the laboratory of Schimmel & Co. had the following properties: $d_{15°}$ 0.9456; $n_{D20°}$ 1.47274; $[\alpha]_{D20°}$ —15°38';

[1]) Bericht von Schimmel & Co. October 1889, 53.

[2]) Report of Schimmel & Co. October 1894, 56.

[3]) Liebig's Annalen 336 (1904), 269.

[4]) *Achillea moschata,* L. was formerly official as *"herba Genippi vel Geneppi veri"*. *"Geneppikraut"* is also used to designate *Achillea nana,* L. and *A. atrata,* L.

[5]) Bericht von Schimmel & Co. April 1889, 43.

[6]) Bull. Soc. chim. III. 31 (1904), 694.

A.V. 6.46; E.V. 89.23, corresponding to 31.23 p.c. ester $CH_3COOC_{10}H_{17}$ or 24.54 p.c. alcohol $C_{10}H_{18}O$; E.V. after acetylation 135.38. Deducting the amount of alcohol that occurs as ester, this amounts to 12.69 p.c. of free alcohol.

The oil is readily soluble in 2 to 2.5 parts of 70 p.c. alcohol. Cooled to —12° it did not congeal. Distillation in vacuum yielded fractions in which the presence of l-*camphene, cineol* and *camphor* was proven. Treated with phthalic acid anhydride, the higher fractions yielded a small amount of an *alcohol* not farther examined. From the saponification liquor, sulphuric acid separated a mixture of fatty acids which, judging from the analysis of the silver salt, contained *caprinic* or *caprylic acid*.

917. Chieh Oil.

From Egypt Schimmel & Co.[1]) obtained an herb to be examined for its volatile oil. It is there known as *Chieh* and occurs in the limestone plateaus of Egypt, Tripolis and presumably also in Arabia. The plant is said to be fully developed in March and thrives ·especially well in wet seasons. The infusion of the herb is used medicinally as emollient and diuretic. Professor Heckel, of Marseilles, who made a botanical examination of the material communicated, with reservation, that it was probably the herb of *Artemisia Herba-alba*. This opinion was substantiated by Dr. Giessler, custodian of the Botanical Institute of the University of Leipzig, who ascertained that it was a variety of the above-mentioned species, namely *A. Herba-alba* var. *densiflora*, Bois.

Steam distillation yielded 1.6 p.c. of a yellowish oil, with a distinct odor of thujone, the examination of which yielded the following results: $d_{15°}$ 0.9192; α_D —5°20′; $n_{D20°}$ 1.45611; A.V. 1.5; E.V. 11.0; E.V. after acetylation 40.7; soluble in 2.6 vol. and more of 70 p.c. alcohol. From the low ester and acetylation values it became apparent that the oil contains only small amounts of saponifiable and alcoholic constituents.

From a second lot of herb[2]) only 0.58 p.c. of oil were obtained which did not differ appreciably from the first. It was brownish-yellow in color and remarkable because of its pungent odor,

[1]) Report of Schimmel & Co. April 1909, 98.
[2]) *Ibidem* October 1909, 25.

which was not so evident in the earlier oil. The thujone- or sage-like odor became apparent only after a time. The principal difference, however, lay in the reversed angle of rotation. The new oil was dextrogyrate, the earlier oil lævogyrate, moreover, the second contained more alcoholic constituents. All of these differences possibly find an explanation in the fact that the first oil was distilled from flowering herb, whereas in the second case the flowers were scarcely developed. The new oil had the following constants: $d_{15°}$ 0.8994; $\alpha_D + 14°5'$; $n_{D20°}$ 1.46684; A. V. 4.6; E. V. 35.0; E. V. after acetylation 163.3; soluble in 1.8 vol. and more of 70 p.c. alcohol with separation of paraffin.

918. Oil of Artemisia annua.

From home-grown, green herb of *Artemisia annua*, L., Schimmel & Co.[1]) obtained 0.29 p.c. of a lemon-yellow oil with an agreeable, refreshing odor that reminded distinctly of basilicum. $d_{15°}$ 0.8912; $\alpha_D - 1°18'$; A. V. 3.8; E. V. 19.2; E. V. after acetylation 44.5; the oil was soluble in 1 to 1.5 vol. of 80 p.c. alcohol, the addition of more solvent causing opalescence and turbidity because of the abundant separation of paraffin.

919. Oil of Artemisia frigida.

From the fresh *Artemisia frigida*, Willd., collected in South Dakota, where it is known as wild sage, F. Rabak[2]) distilled 0.41 p.c. of a greenish oil of cineol-like odor. $d_{22°}$ 0.927; $\alpha_D - 24°48'$; A. V. 1.2; E. V. 31.8; S. V. 33.0. The dried herb upon distillation yielded only 0.07 p.c. of oil of a dark color: $d_{15°}$ 0.930; A. V. 4.7; E. V. 40; S. V. 44.7.

Later the same investigator[3]) described three additional oils. d 0.927 to 0.933; $\alpha_D - 23°40'$ to $- 25°10'$; A. V. 1.2 to 3.0; E. V. 31.8 to 45.0; E. V. after acetylation 139 and 143. With 0.5 vol. and more of 90 p.c. alcohol the oils yielded a clear solution. They had a decided odor of *cineol*, the presence of which was proven qualitatively by the phosphoric acid reaction.

[1]) Report of Schimmel & Co. April 1905, 85.

[2]) Pharm. Review 28 (1905), 128.

[3]) *Ibidem* 24 (1906), 324.

Another oil which was investigated chemically by Rabak[1]) was of the same origin as the preceding ones and had been obtained with a yield of 0.26 p.c. d_{24° 0.940; α_D — 24.2°; n_{D24° 1.4716; soluble in 1 vol. of 80 p.c. alcohol; A.V. 2.5; E.V. 25; E.V. after acetylation 139. From the oil there separated upon standing 3 p.c. of l-*borneol* (m.p. 203°; $[\alpha]_D$ — 32°). Of free acids presumably *caprylic acid* and *œnanthic acid* were present; as esters *œnanthic* and *valeric,* also traces of *formic* and *undecylic acids.* Other constituents are *cineol* 18 to 20 p.c. (m.p. of iodol compound 110 to 113°) and l-*fenchone* 8 to 10 p.c. (m.p. of oxime 164 to 165°). Of borneol there is present a total of 43 p.c. of which 35.6 p.c. is free borneol and 6.8 p.c. as œnanthic ester.

920. Oil of Artemisia Ludoviciana.

Artemisia Ludoviciana, Nutt., also from South Dakota, was likewise distilled by F. Rabak[2]). The fresh herb yielded 0.38 p.c. of a greenish-yellow oil of strongly aromatic odor: d_{22° 0.929; α_D — 16° 14′; A.V. 4; E.V. 10. Three other oils had the following properties: d 0.929 to 0.931; α_D — 13° 32′ to — 17° 20′; A.V. 0 to 4.3; E.V. 10 to 26; E.V. after acetylation 116 (one determination). The oil was soluble in 0.5 vol. and more of 90 p.c. alcohol and yielded a *cineol* reaction with phosphoric acid.

921. Oil of Artemisia caudata.

As in the two previous instances, the material used in the distillation of the oil of *Artemisia caudata,* Michx. was collected in South Dakota by F. Rabak[1]). The fresh herb yielded 0.24 p.c. of a yellow oil with a sweetish odor that suggests the presence of methyl chavicol or anethol. d_{22° 0.920; α_D — 12° 30′; A.V. 0; E.V. 17.0. The constants of three additional oils were determined later[3]): d 0.8418 to 0.920; α_D inactive to — 24° 20′; A.V. 0 to 20; E.V. 17 to 73.

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[1]) U.S. Dep. of Agriculture, Bureau of Plant Industry, Bull. No. 235, p. 21.

[2]) Pharm. Review 23 (1905), 128.

[3]) *Ibidem* 24 (1906), 324.

922. Oil of Artemisia biennis.

From the wilted herb of North American *Artemisia biennis,* Willd., which had almost passed the flowering stage, F. Rabak[1]) obtained 0.03 p.c. of a dark red-brown oil with a sweetish odor and taste: $d_{25°}$ 0.893; $[\alpha]_D + 4.39°$; $n_{D30°}$ 1.5181; A.V. 0; E.V. 16 ·· 5.6 p.c. ester $C_{10}H_{17}CO_2CH_3$; E.V. after acetylation 60 = 17.28 p.c. alcohol $C_{10}H_{18}O$. With 4 vol. and more of 95 p.c. alcohol it yielded a turbid solution. The oil possibly contains *methyl chavicol.*

923. Oil of Artemisia serrata.

Artemisia serrata, Nutt. is also a North American plant. From the fresh, flowering herb Rabak[1]) obtained 0.3 p.c. of reddish-brown oil with an exceedingly bitter taste: $d_{25°}$ 0.913; $\alpha_D + 6.8°$; $n_{D30°}$ 1.4602; A.V. 1.6; E.V. 10 = 3.5 p.c. ester $C_{10}H_{17}CO_2CH_3$; E.V. after acetylation 43 = 12.2 p.c. alcohol $C_{10}H_{18}O$; soluble in $1/2$ vol. of 80 p.c. alcohol. Presumably the oil contains *thujone.*

924. Oil of Artemisia variabilis.

An oil that had been distilled from the flowering herb of *Artemisia variabilis,* Ten. in Reggio, Calabria, was examined by Schimmel & Co.[2]). It was of brown color and its oder reminded of that of petitgrain oil. $d_{15°}$ 0.9115; $\alpha_D - 9° 20'$. Of free acid but little was present (A. V. 1.7), the amounts of ester (E. V. 15.5) and of alcohol (E. V. after acetylation 49.1) were also small. In alcohol the oil was but imperfectly soluble, even in absolute alcohol, the solution which was clear at first, became turbid upon the addition of 10 to 12 vol.

925. Oil of Artemisia cana.

Interesting because of its content of l-*camphor* is the oil distilled by Th. Whittelsey[3]) with a yield of 1.2 p.c. from the fresh branches and leaves of an *Artemisia* species, probably *A. cana,* Pursh. The strongly aromatic plant, which is indigenous to western North America, yields an oil with the following

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[1]) Midland Drugg. and pharm. Review 45 (1911), 283.
[2]) Report of Schimmel & Co. April 1902, 77.
[3]) *Wallach-Festschrift* (Göttingen 1909, Vandenhoeck & Ruprecht) 668.

properties: $d_{15°}$0.9405; α_D — 19.09°; $n_{D20°}$ 1.4702; A. V. 4.1 to 4.2;
S. V. 22.7 to 23.9; S. V. after acetylation 110.3 to 111.8. By
distillation it was resolved into three fractions: I. 185 to 191°;
II. 191 to 197°; III. 197 to 203°. Fraction III consisted for the
most part of l-*camphor* (m. p. 174 to 175°; m. p. of oxime 119
to 120°). Camphor separates even from the original oil when
exposed to the temperature of a freezing mixture. As deter-
mined by means of its semicarbazone (m. p. 235 to 236°) camphor
is present to the extent of at least 44.5 p.c.

926. Oil of Artemisia lavandulæfolia.

In the Botanical Institute at Buitenzórg there has been exa-
mined the oil of a plant growing wild in the Tengger Mts., Java,
which was said to have been derived from *Artemisia lavandulæ-
folia*[1]). According to a later communication[2]), however, it seems
doubtful as to whether the oil was obtained from this plant.
$d_{26°}$ 0.924; α_D — 7° 32′; upon cooling the oil solidified for the most
part. The solid substance, which likewise separates upon the
addition of petroleum ether, melts at 32.5 to 33°, contains a
methoxy group, takes up three molecules of bromine and pro-
bably has the composition $C_{12}H_{14}O_3$. Heated with potassium
hydroxide for two hours, two molecules of alkali were consumed.
Thereupon the reaction mixture was distilled with steam. A sub-
stance having the odor of amyl acetate, possibly methyl heptenone,
passed over. With iodine and potassium hydroxide the distillate
gave a strong iodoform test. After acidification, *n*-butyric acid
distilled over. The solid substance is probably the methyl ester
of a decomposible acid.

927. Oil of Artemisia cœrulescens.

Artemisia cœrulescens, L. grows along the Mediterranean
and Atlantic coasts. It yields the *Erba Santa Maria* of which
Schimmel & Co.[3]) obtained a sample from Turin. They obtained
0.24 p.c. of an oil the odor of which bore a certain resemblance
to that of hyssop oil but at the same time reminded somewhat

[1]) Jaarb. dep. Landb. in Ned.-Indië, Batavia 1907, 66.

[2]) *Ibidem* 1910, 45.

[3]) Report of Schimmel & Co. October 1911, 104.

of ambra. At room temperature it congealed to a brownish, butyraceous mass permeated with crystals. This mass did not melt to a light brownish liquid until heated to 35 to 40°. $d_{15°}$ 0.9179; α_D — 5° 50'; A.V. 11.3; E.V. 42.0; insoluble in 80 p.c. alcohol; soluble in all proportions of 90 p.c. alcohol with the separation of a solid substance. Upon recrystallization from alcohol, the isolated crystals were obtained as white, odorless needles that melted at 108°. They have not been investigated as to their chemical nature.

928. Oil of Petasites officinalis.

The fresh root of *Petasites officinalis*, Mœnch, Ger. *Pestwurz,* yields, upon distillation, 0.1 p.c. of a volatile oil that does not yield a clear solution with even 10 vol. of 90 p.c. alcohol. $d_{15°}$ 0.944; α_D + 2° 18'[1]).

929. Fireweed Oil.

Erechthites hieracifolia, Raf. occurs frequently on burntover areas of North America from Canada to Louisiana and Nebraska[2]). Hence it is known as fireweed. However, the same designation applies to at least six different wild plants, hence a pure fireweed oil from *Erechthites* is rarely to be found in commerce[3]).

According to A. M. Todd[4]) the oil has a specific gravity of 0.845 to 0.855, according to F. B. Power[5]) 0.838 at 18.5°. It is either dextrogyrate or lævogyrate, α_D — 2 to + 2°[5]), according to Todd up to + 4°.

According to F. Beilstein and E. Wiegand[6]) the bulk of the oil consists of a terpene that boils at 175°, has a specific gravity of 0.838 at 18.5°, and absorbs one molecule of hydrogen chloride, without separating a crystalline compound. Fraction 240 to 310° likewise corresponds to the formula $C_{10}H_{16}$.

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[1]) Observation made in the Laboratory of Schimmel & Co.

[2]) A. Henkel, U. S. Department of Agriculture, Bureau of Plant Industry, Bull. No. 219, p. 43.

[3]) L. F. Kebler and G. R. Pancoast, Americ. Journ. Pharm. 75 (1903), 216.

[4]) *Ibidem* 59 (1887), 302.

[5]) Pharm. Rundsch. (New York) 5 (1887), 201.

[6]) Berl. Berichte 15 (1882), 2854.

Acoording to Power the fractions above 190° are to be regarded merely as polymerization products that have resulted from boiling.

930. Oil of Arnica Flowers.

Origin. Upon distillation, the flowers of *Arnica montana,* L. yield but a very small amount, 0.04 to 0.07 p. c. of volatile oil.

Properties. The oil of arnica flowers has a reddish-yellow to brown color and a strong, aromatic odor and taste. At middle temperatures it commonly constitutes a butyraceous mass which melts between 20 and 30° to a brownish liquid. $d_{30°}$ 0.8905 to 0.9029; A.V. 62.6 to 127.3; E.V. 22.7 to 32.2.

In alcohol the oil is very difficultly soluble. Even the solutions in absolute alcohol are clear only in the beginning[1].

Composition. The oil itself has not been examined thus far. In the petroleum ether extract of the flowers B. Börner[2] found *lauric* and *palmitic acids,* also· hydrocarbons of the paraffin series. Inasmuch as all three substances are volatile with water vapor they must be contained in the oil. Unquestionably they are the cause of the congealing of the oil. Schimmel & Co. isolated from the oil an acid melting at 61°.

According to the investigations of Klobb, Garnier and Ehrwein[3], arnica flowers contain a *paraffin* $C_{30}H_{62}$ that melts at 62°, which presumably is contained in the oil.

931. Arnica Root Oil.

Origin and Production. From the recently dried root of *Arnica montana,* L. 0.5 to 1.5 p.c. of oil are obtained. At first it is light yellow in color but darkens with age. Its odor reminds of radish, and its taste is pungent and aromatic. $d_{15°}$ 0.982 to 1.00; $\alpha_D + 0°25'$ to — 2°; $n_{D20°}$ 1.507 to 1.508; A.V. 4 to 10; E.V. 60 to 100; soluble in 7 to 12 vol. of 80 p.c. alcohol and in 0.5 to 6 vol. of 90 p.c. alcohol, in both cases the solutions are turbid at times[1].

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[1] Report of Schimmel & Co. April 1913, 28.
[2] Inaug.-Dissertation. Erlangen 1892.
[3] Bull. Soc. chim. IV. 7 (1910), 940.

Composition. Arnica root oil was first investigated by G. F. Walz[1]) who stated that the bulk of the oil consisted of capronic acid hexyl ester, $C_{12}H_{24}O_2$, and that the aqueous distillate contained capronic and caprylic acids. Very different were the results obtained by O. Sigel[2]). In the aqueous distillate he found *isobutyric acid,* also very little *formic acid* and a small amount of an acid the silver salt of which yielded results corresponding with angelic or valeric acids.

The oil distilled with decomposition between 214 and 263° and left a brown, resinous residue.

For the purpose of examining individual constituents, the oil was saponified with alcoholic potassa. 'From the alkaline solution neutralization with dilute sulphuric acid separated a phenol that boiled between 224 and 225° and had a specific gravity of 1.015 at 12°. Its analysis agreed with the formula $C_8H_{10}O$ and Sigel declared it to be *phlorol* (ethyl phenol) without, however, supplying further proof for this assumption. The ethyl ether of this phenol is a colorless liquid of agreeably aromatic odor, specific gravity 0.9323 at 18° and boils at 215 to 217°.

The alkaline saponification liquid contained, in addition to this phenol, *iso*butyric acid. This renders it probable that the original oil contains *phlorol* iso*butyric ester.*

The oil separated with water from the alcoholic potassa solution boiled between 224 and 245° and upon oxidation with chromic acid, yielded thymoquinone, $C_{10}H_{12}O_2$. Heated with hydrogen iodide in a sealed tube, there were obtained methyl iodide, thymohydroquinone, $C_{10}H_{14}O_2$, also a phenol boiling at 225 to 226° and of the composition of a phlorol, $C_8H_{10}O$. This leads to the conclusion that the oil contains *thymohydroquinone dimethyl ether* and *phlorol methyl ether.*

According to Sigel's investigations arnica root oil consists of one-fifth of the iso*butyric acid phloryl ester,* the remaining four-fifths consisting of the *methyl ether of thymohydroquinone* with small amounts of the *methyl ether of phlorol.*

[1]) Neues Jahrbuch der Pharmacie 15 (1861), 329. — Arch. der Pharm. 158 (1861), 1. — Jahresber. d. Chem. 1861, 752.

[2]) Liebig's Annalen 170 (1873), 345.

I. Kondakov[1]) isolated from the oil an unsaturated hydro-carbon boiling at 176 to 180°, a solid substance melting at 69° and a sulphur-containing substance. The presence of *iso*butyryl phlorol and dimethyl-thymohydroquinone found by Sigel[2]), was verified by him.

932. Oil of Carlina acaulis.

Origin and Production. The root of *Carlina acaulis*, L., Ger. *Eberwurz*, yields upon distillation[3]) 1.5 to 2.1 p.c. of a light to dark brown oil with a narcotic odor reminding somewhat of *Fœnum græcum*. $d_{15°}$ 1.032 to 1.037; α_D — 3° 30′ to — 7° 5′; $n_{D20°}$ 1.5567 to 1.5696; A. V. 2.5; E. V. 4,3; E. V. after acetylation 13.1 (one determination in each case); soluble in 4 vol. of 90 p.c. alcohol. Occasionally the oil separates crystalline laminæ[4]) of palmitic acid in the cold.

Composition. As shown by F. W. Semmler[5]) carlina oil contains 12 to 15 p.c. of a monocyclic sesquiterpene which he named *carlinene:* $d_{22.8°}$ 0.8733; n_D 1.492; b.p. 250 to 253° (760 mm.), 139 to 141° (20 mm.).

From the high boiling portions of the oil, *palmitic acid,* b.p. 62°, separated.

The principal constituent of carlina oil is *carlina oxide* $_{18}H_{10}O$ (b.p. 167 to 168° under 20 mm. pressure: $d_{17°}^{47°}$ 1.066; $_D$ 1.586; $\alpha_D + 0°$). Oxidized with potassium permanganate it ielded a large amount of benzoic acid. Reduction with sodium nd alcohol produced its tetrahydroderivative $C_{18}H_{14}O$, which pon oxidation with potassium permanganate yielded γ-phenyl-utyric acid $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$ (m.p. 52°). In that portion f the molecule removed by oxidation Semmler suspected a irane ring. Hence the substance $C_{18}H_{11}O$ ought to have been -phenyl-3-α-furylpropane: —

$$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C \overset{\displaystyle HC - CH}{\underset{\displaystyle O}{\Big\| \quad \Big\|}} CH$$
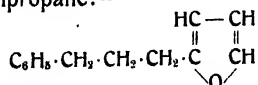
1) Journ. f. prakt. Chem. II. 79 (1909), 505.
2) Liebig's Annalen 170 (1873), 345.
3) Bericht von Schimmel & Co. April 1889, 44.
4) H. Haensel, Apotheker Ztg. 17 (1907), 275.
5) Chem. Ztg. 13 (1889), 1158: Berl. Berichte 39 (1906), 726.

A synthesis verified this assumption and proved the identity of both substances. The synthesis was affected by condensation of acetophenone and furfurol by means of potassa and subsequent reduction of the condensation product.

$$C_6H_5 \cdot CO \cdot CH_3 + OHC \cdot C \underset{O}{\overset{HC-CH}{\underset{||}{\overset{||}{}}}} CH \rightarrow C_6H_5 \cdot CO \cdot CH = CH \cdot C \underset{O}{\overset{HC-CH}{\underset{||}{\overset{||}{}}}} CH \rightarrow$$

$$C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot C \underset{O}{\overset{HC-CH}{\underset{||}{\overset{||}{}}}} CH \rightarrow C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C \underset{O}{\overset{HC-CH}{\underset{||}{\overset{||}{}}}} CH.$$
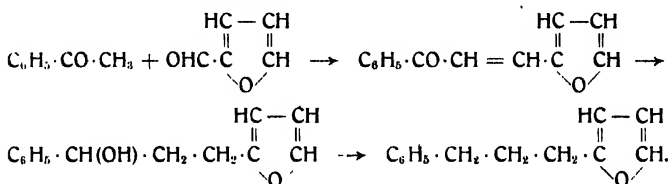
If the last formula expresses the constitution of tetrahydro-carlinaoxide, carlina oxide itself must have one of the following formulas: —

$$C_6H_5 \cdot C{:}C{:}C \underset{O}{\overset{HC-CH}{\underset{H\ H}{\overset{||\ \ ||}{}}}} CH \qquad C_6H_5 \cdot C \underset{O}{\overset{HC-CH}{\underset{H_2}{\overset{||\ \ ||}{}}}} C{-}C{-}C \ CH \qquad C_6H_5 \cdot C \cdot C \underset{O}{\overset{HC-CH}{\underset{H_2}{\overset{||\ \ ||}{}}}} = C \cdot C \ CH$$
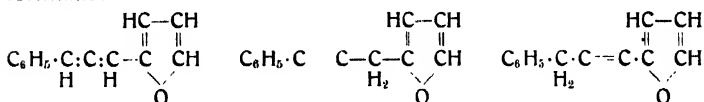
In order to decide between these three formulas, F.W.Semmler and E. Ascher[1]) tried to synthesize carlina oxide but did not succeed. However, they were successful in synthesizing dihydro-carlina oxide, the properties of which occupy an intermediate position between those of carlina oxide and tetrahydrocarlina oxide.

Heretofore it was assumed that furfurol in volatile oils owes its origin to the decomposition of carbohydrates. Now that it has been shown that the principal constituent of carlina oil is a furane derivative, Semmler is of the opinion that the older view requires modification, at least to the extent that furfurol, at least in part, may be derived from compounds of the type to which carlina oxide belongs.

According to J. Gadamer and T. Amenomiya[2]) the oil contains a trace of a *phenol* that is colored orange by ferric chloride.

933. Oil of Burdock.

Arctium lappa, L., Ger. *grosse Klette,* contains a volatile oil in the root as well as in the leaves[3]). From the root the

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[1]) Berl. Berichte 42 (1909), 2355.

[2]) Arch. der Pharm. 241 (1903), 44.

[3]) H. Haensel, Apotheker Ztg. 18 (1903), 744; 19 (1904), 557.

oil was obtained with a yield of 0.065 to 0.176 p.c. It congeals at lower temperature. $d_{22°}$ 0.8925; $d_{35°}$ 0.8808; $d_{25°}$ 0.9695; $\alpha_{D80°} + 1.24°$; A.V. 13.5 to 109; S.V. 109 to 236.6. The only known constituent is *palmitic acid* (m.p. 62°; silver salt).

The dried leaves yield upon distillation 0.0285 p.c. of a dark brown oil. $d_{20°}$ 0.9562; α_D slightly dextrogyrate; A.V. 76; S.V. 91.5. It seems also to contain *palmitic acid.*

934. Costus Root Oil.

Origin. Costus root, which is used in perfumery and which is characterized by a peculiar odor, is derived from *Saussurea Lappa,* Clarke (*Aplotaxis Lappa,* Decaisne; *A. auriculata,* D.C.; *Aucklandia Costus,* Falconer). It should not be confounded with the root of *Costus speciosus,* Smith, family *Scitaminaceæ,* which is odorless and which is used as vegetable being boiled like potatoes[1]).

Saussurea Lappa is a large, luxuriant, herbaceous plant, which is indigenous to the northern Himalayas, where it occurs at altitudes of from 7000 to 13000 feet. The root is fully developed in fall and is collected in September and October. In Cashmere as many as two million pounds are said to be collected annually. They are used principally to protect the shawls made in Cashmere against insects[2]). Large quantities are exported to China where, under the name of *putchuk,* it is used in fumigation[3]). Upon distillation costus root yields 0.3 to 1 p.c. of volatile oil, in one instance a yield of 2.78 p.c. has been recorded[4]).

Properties. The oil of costus root is viscid, and of a light yellow to brown color[5]). The odor at first suggests elecampane[6]), but later an agreeable violet-like odor becomes apparent. The oil from old roots is sometimes possessed of a disagreeable goat odor. $d_{15°}$ 0.940 to 1.009; $\alpha_D + 13$ to $+26°$; A.V. 8 to 24; E.V. 55

[1]) D. Hooper, The Agricultural Ledger 1906, No. 2, p. 69

[2]) Sawer, Odorographia. 1892. Vol. I. p. 109.

[3]) Flückiger, *Pharmakognosie.* III. ed., 1891, p. 481. — Guibourt, Histoire des drogues simples. 1869. Vol. 3, p. 25. — G. Watt, The commercial products of India. London 1908, p. 980.

[4]) D. Hooper, Board of scientific advice for India 1911 to 1912, 31.

[5]) Report of Schimmel & Co. April 1896, 20.

[6]) Even during antiquity elecampane was used to adulterate costus.

to 110; S.V. 67 to 115; E.V. after acetylation 105 to 162; soluble in 90 p.c. alcohol, at first the solution is clear, but upon addition of about 2 vol. of solvent opalescence and even turbidity (paraffin) results, which is observable with larger amounts of 95 p.c. alcohol.

Two oils from roots obtained from the Punjab were semi-solid to solid at ordinary temperature and were permeated with crystals of naphthalene (see under Composition)[1]).

Composition. The oil has been carefully examined by F. W. Semmler and J. Feldstein[2]). Its behavior toward sodium hydroxide caused them to suspect the presence of a lactone. As a matter of fact a lactone was found in fraction 200 to 210° (11 mm.) ($d_{21°}$ 1.0749; $\alpha_{D} + 38°$; n_{D} 1.53103). It was purified through its hydroxy acid and its methyl ester. The latter, upon boiling, again yielded the *costus lactone*. It has the composition $C_{15}H_{20}O_2$, boils at 205 to 211° (13 mm.); $d_{21°}$ 1.0891; $\alpha_{D} + 28°$; n_{D} 1.53043; mol. refr. computed for $C_{15}H_{20}O_2/_2$ 65.71, found 65.85. Costus lactone is bicyclic with two double bonds.

Fraction 190 to 200° (11 mm.) ($d_{21°}$ 1.0501; $\alpha_{D} + 44°$; n_{D} 1.52703) contained a dicyclic acid $C_{15}H_{22}O_2$ with two double bonds, which was named *costus acid* and which, after purification by means of its silver salt, showed the following properties: b.p. 200 to 205° (11 mm.); $d_{21°}$ 1.0508; $\alpha_{D} + 40°$; n_{D} 1.51912; mol. refr. computed for $C_{15}H_{22}O_2/_2$ 67.85, found 67.73. Its methyl ester boiled at 170 to 175° (11 mm.).

The same fraction contained a lactone $C_{15}H_{22}O_2$ which the authors named *dihydrocostuslactone*. The silver salt of the corresponding acid was converted into the methyl ester, from which distillation in vacuum regenerated dihydrocostuslactone. Thus purified it showed the following properties: b.p. 210 to 213° (19 mm.); $d_{22°}$ 1.0776; $\alpha_{D} + 48°$; n_{D} 1.52289; mol. refr. computed for $C_{15}H_{22}O_2/$ 66.31, found 66.31. This dihydrocostuslactone can be obtained from costus acid by heating with 33 p.c. sulphuric acid. Upon hydrogenation with platinum-hydrogen, both the costuslactone and the dihydrocostuslactone yield the same tetrahydrocostuslactone $C_{15}H_{24}O_2$, b.p. 198 to 202° (13 mm.);

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[1]) Observation made in the Laboratory of Schimmel & Co.
[2]) Berl. Berichte 47 (1914), 2433, 2687.

$d_{21°}$ 1.0451; $\alpha_D + 33°$; n_D 1.50510; mol. refr. computed for $C_{15}H_{24}O_2$ 66.71, found 66.99. Costuslactone, dihydrocostuslactone and costus acid are genetically related: 1. costus acid can be changed to dihydrocostuslactone, 2. costuslactone and dihydrocostuslactone can be converted into the tetrahydrocostuslactone mentioned above. They probably belong to the bicyclic terpene type of the sesquiterpene class. Costuslactone is isomeric with alantolactone.

Fraction 175 to 190° (11 mm.) (d_{21} 1.0082; $\alpha_D + 33°$; n_D 1.51962) contained a bicyclic primary sesquiterpene alcohol, $C_{15}H_{24}O$, with two double bonds for which the name *costol* was proposed. It reacts readily with phthalic acid anhydride. Regenerated for the acid phthalic ester, it boils at 169 to 171° (11 mm.); $d_{21°}$ 0.9830; $\alpha_D + 13°$; n_D 1.52000; mol. refr. computed for $C_{15}H_{24}O/_2$ 67.67, found 67.9. Oxidized in glacial acetic acid solution with chromic acid, costol is converted into an aldehyde, the semi-carbazone of which melts at 217 to 218°. Theoretically this aldehyde should have a density of 0.99, in reality its density is 0.9541 at 22° (b.p. 164 to 165° under 15 mm. pressure; $\alpha_D + 24°$; n_D 1.50645), hence it is assumed that a rearrangement has taken place in the course of the oxidation. With phosphorus trichloride costol yields costylchloride, $C_{15}H_{23}Cl$, b.p. 160 to 165° under 13 mm. pressure. Upon reduction with sodium and alcohol this chloride is converted into the sesquiterpene *iso*costene: b.p. 130 to 135° (12 mm.); $d_{21°}$ 0.9062; $\alpha_D + 31°$; n_D 1.50246; mol. refr. computed for $C_{15}H_{24}/_2$ 66.15, found 66.37. This *iso*costene appears to be a sesquiterpene of the caryophyllene type with two double bonds. Upon reduction of costus acid methyl ester with sodium and alcohol costol was obtained.

Fraction 160 to 175° (11 mm.) ($d_{21°}$ 0.9235; $\alpha_D + 14°$; n_D 1.49994) contained a hydrocarbon $C_{17}H_{28}$ (?) to which the name *aplotaxene* was given. It boiled at 154 to 156° (11 mm.) and showed a low density, namely, 0.8604 at 21°. However, it was impossible to obtain it absolutely free from oxygenated constituents. Reduction with sodium and alcohol yielded dihydroaplotaxene, $C_{17}H_{30}$ (b.p. 154 to 157°; $d_{21°}$ 0.8177), which upon reduction with hydrogen and platinum sponge was converted into octohydroaplotexene (b.p. 159 to 163° under 11 mm. pressure; $d_{16°}^{21°}$ 0.7805). The latter is, no doubt, identical with n-hepta-

decane. From this it follows that aplotaxene is an aliphatic hydrocarbon with normal chain which contains four double bonds, two of which are in conjugated position.

Fractions 100 to 130° (11 mm.) and 130 to 150° (11 mm.) contained two sesquiterpenes, which were designated α- and β-costene.

α-Costene boiled between 122 and 126° (12 mm.); $d_{21°}$ 0.9014; α_D —12°; n_D 1.49807; mol. refr. computed for $C_{15}H_{24}/_2$ 66.15, found 66.37. When hydrated according to Bertram and Walbaum an alcohol boiling between 150 and 165° (14.5 mm.) resulted.

β-Costene boiled between 144 and 149° (18 mm.); $d_{22°}$ 0.8728; α_D +6°; n_D 1.4905; mol. refr. computed for $C_{15}H_{24}/_3$ 67,86, found 67.65.

Finally fraction 60 to 100° (11 mm.) was examined. It contained *phellandrene* (m.p. of bisnitrosite 106 to 108°), *camphene* (conversion into *iso*borneol), and probably a terpene alcohol $C_{10}H_{16}O$.

The percentage composition of costus oil may be approximated as follows: —

About 0.4 p.c. camphene, 0.4 p.c. phellandrene, 0.2 p.c. terpene alcohol, 6 p.c. α-costene, 6 p.c. β-costene, 20 p.c. aplotaxene, 7 p.c. costol, 15 p.c. dihydrocostuslactone, 11 p.c. costuslactone and 14 p.c. costus acid.

In two samples of semisolid and solid consistence, which D. Hooper had sent from Calcutta, Schimmel & Co. showed the presence of *naphthalene* (m.p. 79°; m.p. of picrate 149°).

935. Oil of Dandelion.

From the alcoholic extract of dandelion, *Taraxacum officinale,* Web., F. B. Power and H. Browning, Jr.[1] obtained traces of a dark yellow, volatile oil in which they proved the presence of *furfurol* by means of a color reaction.

[1] Journ. Chem. Soc. 101 (1912), 2413.

Oils of Unknown Botanical Origin.

936. Balan Oil.

As communicated by Schimmel & Co [1]) the volatile oil known as balan oil[2]) is obtained from a small shrub with green flowers. Parts of this plant are used by the native Javanese as anthelmintic with both man and animals. In certain districts it is also used in one form or another as a remedy in nervous diseases. The oil obtained with a yield of 0.05 p.c. is brown in color. Its odor reminded somewhat of orange oil and gave the following constants: $d_{15°}$ 0.9042; $n_{D20°}$ 1.47715; A.V. 13.0; E.V. 20.5; soluble in $^1/_2$ vol. and more of 90 p.c. alcohol. On account of its dark color the optical rotation could not be determined with certainty. In all probability the angle is very small. With sodium acid sulphite the oil reacted forming a solid compound, from which there was regenerated a compound having the odor of decylic aldehyde. Its semicarbazone melted at 152°. The aldehyde was presumably a mixture.

937. Quipita Wood Oil.

In Venezuela the name quipita wood is applied to a relatively light colored, very dense wood, which enters commerce in pieces several meters long and from 5 to 10 cm. thick. The thicker stems have a thin white outer bark, somewhat resembling birch stems, the bark of the younger stems is grayish-brown.

Upon distillation of the rasped wood Schimmel & Co.[3]) obtained 1 p.c. of a light yellow oil the odor of which reminded of turpentine oil: $d_{15°}$ 0.934; α_D — 34° 31'; S.V. 2.9; S.V. after acetylation 40.2. This shows that in addition to very small amounts of esters alcoholic constituents are likewise present.

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[1]) Report of Schimmel & Co. April 1911, 123.

[2]) According to F. S. A. de Clercq (*Nieuw plantkundig Woordenboek voor Nederlandsch Indië*, Amsterdam 1909, p. 254) the Javanese designate *Heritiera littoralis*, Ait. *(Sterculiaceæ)* as *Balang pasisir.*

[3]) Report of Schimmel & Co. October 1896, 71.

938. Oil of False Camphor Wood or Hazamalanga Wood.

In 1910 Schimmel & Co.[1]) obtained from Madagascar a wood named *faux camphrier*[1]), which upon distillation yielded 2 p.c. of a volatile oil. The latter contained 75 p.c. of an aldehyde, which turned out to be the dextrogyrate form of perilla aldehyde (see p. 560). Endeavours to ascertain the botanical origin of the wood were unsuccessful at first. Later the firm obtained samples of the same wood from other sources. In one instance it was named *bois de cass,* in another *hazamalanga wood.* The source was given as Madagascar where it is used as building material proof against termites. Still later other parts of the plant were obtained thus enabling Dr. Giessler, custodian at the Botanical Institute of the University at Leipzig, to identify it as *Hernandia peltata,* Meissn., family *Hernandiaceæ.*

Properties[2]). Four samples of trunk wood yielded between 1.03 and 2.06 p.c. of oil with the following properties: $d_{15°}$ 0.958 to 0.963; $\alpha_D + 83°45'$ to $+104°12'$; $n_{D20°}$ 1.49695 to 1.50111; soluble in 2.5 to 4 vol. and more of 70 p.c. alcohol, in one instance with slight opalescence. With sodium acid sulphite these and the other oils did not react quantitatively, but with neutral sulphite they did. Thus between 75 and 80 p.c. of aldehyde was found present. The acid value for one oil was 4.4, the ester value 47.1.

The wood from the roots yielded 0.5 p.c. of oil with the following properties: $d_{15°}$ 0.9667; $\alpha_D + 126°15'$; $n_{D20°}$ 1.50383; aldehyde content (sulphite method) 92.5 p.c.; soluble in 2.5 vol. and more of 70 p.c. alcohol.

The oil obtained with a yield of 0.5 p.c. from the entire fruit had the following properties: $d_{15°}$ 0.9528; $\alpha_D + 50°16'$; $n_{D20°}$ 1.49554; aldehyde content (sulphite method) 49 p.c.; soluble in 0.3 vol. and more of 90 p.c. alcohol, of 80 p.c. alcohol 10 vol. were insufficient

Much more oil was contained in the almond-like seeds, namely 1.38 p.c.; $d_{15°}$ 1.0044; $\alpha_D + 87°$; $n_{D20°}$ 1.50614; A. V. 7.3; E. V. 110.4 not completely soluble in 10 vol. of 70 p.c. alcohol; soluble in 0.5 vol. of 80 p.c. alcohol, more alcohol causing opalescence. The aldehyde content was high but could not be determined for want of sufficient material.

[1]) Report of Schimmel & Co. October 1910, 146.
[2]) *Ibidem* April 1915, 51.

All of the oils were of a pale to dark yellow color and with the exception of the oil from the entire fruit, had the characteristic odor of perilla aldehyde.

Composition. F. W. Semmler and B. Zaar[1]), to whom the oil from the wood was submitted, found that the aldehyde contained in the oil is identical with d-*perilla aldehyde*. This was demonstrated by its conversion into *d*-limonene, by the preparation of its oxime and the oxidation to perillic acid. The *d*-perilla aldehyde, isolated by means of the bisulphite compound, showed the following properties: b.p. 99 to 104" (9 mm.) $d_{18°}$ 0.965; $[\alpha]_D + 135.6°$; n_D 1.50803.

Besides *d*-perilla aldehyde the oil contains *myrtenal,* an aldehyde which F. W. Semmler and K. Bartelt[2]) had prepared by the oxidation of myrtenol and concerning the occurrence of which in volatile oils nothing had been known. For the purpose of isolating the myrtenal, the oil was shaken with neutral sodium sulphite solution. From the sulphite solution made alkaline, the aldehyde was distilled over with steam, in which operation the perilla aldehyde remained in solution. The purified myrtenal had the following properties: b.p. 89 to 92° (11 mm.), $d_{20°}$ 0.9859; $[\alpha]_D + 13.6°$; n_D 1.50618. The semicarbazone melted at 230°. From the myrtenaloxime (b.p. 125 to 128° under 9 mm. pressure; $d_{21°}$ 1.0292; $[\alpha]_D + 42°$; n_D 1.53803) the authors prepared myrtenalnitrile which, upon saponification, yielded myrtenic acid; m.p. 54°, b.p. 149 to 152° (9 mm.); $d_{22°}$ 1.0712; n_D 1.50618.

Myrtenal.

Perilla aldehyde.

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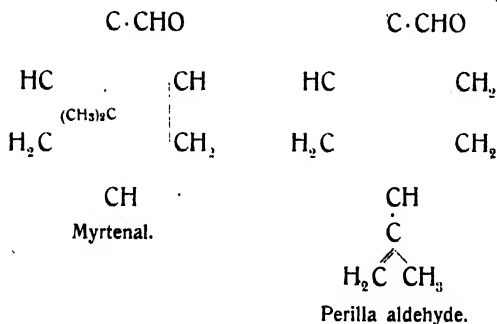
[1]) Berl. Berichte 44 (1911), 815.

[2]) *Ibidem.* — Comp. vol. I, p. 392.

The simultaneous occurrence of perilla aldehyde and myrtenal in the false camphor wood oil is very interesting, since the two aldehydes stand in the same relation to each other as do pinene and limonene.

Additional constituents of the oil are: *cineol* (resorcinol compound) and d-*limonene* (m.p. of tetrabromide 103 to 104°).

939. Cape Oil.

From the Ivory Coast, Roure-Bertrand Fils[1]) obtained leaves which are there known as *cape* and which, upon distillation, yielded 0.28 p.c. of a very mobile, greenish-yellow oil, with an exceedingly strong pleasant odor which at first reminds of patchouly. It had the following properties: $d_{15°}$ 0.977; $\alpha_D + 39°38'$; A.V. 0.7; S.V. 109.2; soluble in an equal volume of 80 p.c. alcohol, the addition of more solvent causing turbidity.

Later[2]) the cape leaves were subjected to a botanical examination by E. G. and A. Camus. It was shown that they belonged to a hitherto unknown species of *Popowia* (family *Anonaceæ*) which the authors named *P. Capea. P. Capea*, E. G. et A. Camus is a creeping shrub which occurs exclusively in the dense forests of the eastern part of the Ivory Coast, in Attié and Agnis, and even in these countries relatively rarely. Strangely, the fruits do not commonly contain seeds, for they are mostly converted into galls by the sting of insects. *Popowia Capea* is used to but a limited extent along the Ivory Coast. A small package of dried leaves of about 200 g. costs 20 cents on the spot, a price which is increased appreciably in the markets outside of the *cape* zone. The crude material, consisting of dried stems and leaves is coarsely comminuted and macerated with cold water. The extract thus obtained is added to the baths.

From about 42 kg. of leaves 246 g. (= 0.59 p.c.) of volatile oil were obtained, the larger part of which (160 g.) was heavier than water. The constants of total oil, as well as of the heavy and light oils are herewith tabulated: —

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[1]) Berichte von Roure-Bertrand Fils October 1911, 43.

[2]) *Ibidem* October 1913, 3.

	Total oil	Heavy oil	Light oil
d_{200}	1.0042	1.0081	0.9960
α_D	$+76°56'$	$+90°54'$	$+51°26'$
A. V.	2.8	1.5	3.7
S. V.	166.1	192.3	123.2
S. V. after acetyl.	239.9	248.3	218.4
Solubility in 80 p.c. alcohol	1 vol., later turbidity	1 vol., later very decided turbidity	1 vol., later decided turbidity
Solubility in 95 p.c. alcohol.	0.5 vol., later slight opalescence.	after 3 vol. distinct turbidity.	0.5 vol., later very light turbidity.

Upon acetylation the angle of rotation is greatly reduced: that of the total oil to $+13°48'$; that of the heavy oil to $+18°4'$ and that of the light oil to $+5°12'$.

6 p.c. of the oil combines with bisulphite.

From the saponification lye a thick oily liquid was obtained which had a distinct odor of cinnamic alcohol, but which did not crystallize.

940. Oil of Paolo amarello.

From the wood known in Brazil as *paolo amarello,* the botanical origin of which is not known, Roure-Bertrand Fils[1]) obtained 0.41 p.c. of an oil that was almost colorless and had an odor like linaloe oil. $d_{15°}$ 0.8892; α_D $-5°54'$; S. V. 22.9; ester content 8 p.c. computed as linalyl acetate; E. V. after acetylation 200.2; soluble in 2 vol. and more of 70 p.c. alcohol.

941. Oil from Turpentine Amarello.

A wood, known in Brazil as *turpentine amarello,* has been distilled by Roure-Bertrand Fils[1]). The shavings yielded 0.1347 p.c. of oil the odor of which reminded of turpentine. α_D $+8°32'$; soluble in all proportions of 90 p.c. alcohol.

942. Gouft Oil.

Distillation of a plant growing on the plateaus of Algeria yielded a light yellow oil, known as gouft oil, which had an odor that reminded of turpentine and mastic. It was examined by P. Jeancard and C. Satie[2]). $d_{9.5°}$ 0.8720; α_D $-15°20'$; A. V. 1.12;

[1]) Berichte von Roure-Bertrand Fils October 1910, 41.

[2]) Bull. Soc. chim. III. 31 (1904), 478.

E. V. 14; E. V. after acetylation 42. It boiled around 170°. The fraction boiling below 170° seemed to contain α-*pinene* (m.p. of nitrosochloride 103°). From the higher boiling fractions a few drops of an alcohol having the odor of *geraniol* were isolated with the aid of phthalic acid anhydride.

943. Sheih Oil.

The sheih oil described by P. Jeancard and C. Satie[1]) was obtained like the preceding oil from Algeria and had likewise been distilled from the entire plant. Its color was brownish-red and its odor was wormwood-like. $d_{9.5}$ 0.9540; A.V. 8.4; E.V. 66.5; E.V. after acetylation 129.5. This oil contained about 15 p.c. phenols, the principal constituent of which was the *dimethylether of pyrogallol* (m.p. 51°; m.p. of benzoate 107 to 108°). The oil deprived of phenols distilled between 175 and 200° and apparently contained *thujone* (m. p. of oxime 54°) and *thujylalcohol*.

944. Maali Oil.

In 1907 Schimmel & Co.[2]) obtained from the German Governor of Samoa an elemi-like balsam labled *Ma'ali*-resin[3]) which, upon distillation with water vapor, yielded 16 p.c. of a light green oil, that solidified at ordinary temperature. According to H. Thoms[4]) the tree known in Samoa as *Maali* or *Mafoa* is *Canarium samoense*, Engl. (family *Burseraceæ*).

Maali oil has a slightly balsamic odor, reminding somewhat of tea roses. $α_D + 7° 15'$; S. V. 3.3; E. V. after acetylation 46.6; soluble in 1 vol. of 90 p.c. and in 3 vol. of 80 p.c. alcohol. It liquified between 65 and 80°. In spite of the high alcohol content the acetylation value is low because when heated with acetic acid anhydride, water is split off and a sesquiterpene is formed, about which more below.

Suction applied to the crystalline paste yielded a colorless and odorless crystalline mass. Recrystallized from either 70 p.c. alcohol

[1]) Bull. Soc. chim. III. 31 (1904), 478.

[2]) Report of Schimmel & Co. November. 1908, 137.

[3]) In Samoa Ma'ali resin is used for stiffening the hair and for embalming the corpses of high chiefs. O. Thiele, *Über wirtschaftliche Verwertung ethnologischer Forschungen*. Tübingen 1906, p. 36, Footnote.

[4]) Notizbl. bot. Garten Berlin 27 (1901), 137; Apotheker Ztg. 16 (1901), 822.

or petroleum ether long needles with silky lustre were obtained which had the following properties: m. p. 105°; $[\alpha]_{D}$ + 18.333°; b. p. abt. 260°; E. V. after acetylation 16.0 (a sesquiterpene results); readily soluble in alcohol, petroleum ether, benzene and other organic solvents. With phenyl *iso*cyanate no phenyl urethane resulted even upon long standing. Neither did semicarbazide or bisulphite react. Concentrated formic acid, however, caused liquifaction even in the cold, the reaction mixture becoming turbid due to the formation of water. The substance in question is, therefore, a sesquiterpene alcohol, elementary analysis indicating the formula $C_{15}H_{26}O$.

When this *maali alcohol* is heated with dehydrating agents, preferably with concentrated formic acid, the corresponding *maali sesquiterpene*, $C_{15}H_{24}$, with the following constants results: $d_{15°}$ 0.9190; α_{D} + 121°20′; $[\alpha]_{D}$ + 131.99°; n_{D} 1.52252; mol. refr. 67.98; b. p. 270.8 to 271.0° (754 mm.); soluble in about 9 vol. and more of 95 p.c. alcohol. The solution of the sesquiterpene in glacial acetic acid is colored indigo blue by a few drops of concentrated sulphuric acid. The analysis yielded results corresponding with the formula $C_{15}H_{24}$.

A nitrosochloride or a nitrosate could not be obtained, neither addition products of hydrogen chloride nor hydrogen bromide, also of water.

When maali alcohol is heated with a concentrated aqueous solution of bichromate that has been slightly acidulated with sulphuric acid, it goes partly into solution, but upon cooling again separates as a dark reddish-brown, crystalline chromium compound[1]). This substance can also be obtained when about 5 g. of the alcohol are introduced into about 50 cc. of a 15 p.c.

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[1]) In connection with maali alcohol Schimmel & Co. (*loc. cit.* 139, footnote) have investigated the behavior of a number of sesquiterpene alcohols toward chromic acid. In most cases they observed combination. Frequently, as in the case of sandalwood oil, these are either thick oils or readily decomposed into their components. Hence, in the pure state they could be obtained only in connection with a few sesquiterpene alcohols. Patchouly alcohol yielded with chromic acid a product in the form of reddish-brown needles that melted at 52 to 53°. The sesquiterpene alcohol of the oil of *Eucalyptus Globulus* melting at 88.5° (see p. 249) yielded orange-red needles that melted at 78°. Ledum camphor yielded brick-red crystals. Other alcohols, such as kesso alcohol, crystallized unchanged even from concentrated solutions of chromic acid.

aqueous solution of chromic acid and digested with slow heating and frequent agitation. If this reaction mass is recrystallized from alcohol or petroleum ether it yields handsome purple, long, thick needles; with more rapid crystallization delicate brick-red needles that melt at 111°. Schimmel & Co. regarded this compound as addition product $(C_{15}H_{26}O)_2 CrO_3$. Since, however, H. Wienhaus[1]) has proven that certain tertiary alcohols, such as ledum camphor and patchouly alcohol, yield chromates of the formula $(C_{15}H_{26})_2 CrO_4$, it may be assumed that this compound of maali alcohol has a like composition.

945 and 946. Shô-Gyū and Yu-Ju Oils.

SHÔ-GYŪ OIL.

In many parts of Formosa there occurs a tree which, according to K. Nagai[2]), bears great resemblance to the camphor tree, yet differs from it botanically, also as to the composition of the oil. The natives call it *Gu Chiu*. As to its botanical position little is known except that it probably belongs to the family *Lauraceæ*. The "black camphor tree" appears to be identical with this tree. So long as its flowers have not been collected and examined it will be impossible to ascertain its botanical name. The leaves of the *Shô-Gyū* tree are much thicker and have a darker green color than that of the camphor leaves. Inasmuch as the leaf-bearing branches frequently are so high that they can be reached only with difficulty, the trees are best identified by scraping off some of the woody tissue, preferably from the roots. The odor reveals at once whether the tree is a camphor tree or a *shô-gyū* tree. The oil is obtained from the wood with a yield of 1.3 to 3 p.c. (an average of 2.5 p.c.). A total annual production of 600000 kin would readily be possible. The oil has the following properties: d 0.900 to 1.031; $\alpha_D + 7.75$ to $+ 30°$; n_D 1.4750 to 1.51302; A. V. 0.1 to 0.96; E. V. 0 to 2.40; E. V. after

[1]) Berl. Berichte 47 (1914), 322.

[2]) Investigation of the Shô-Gyū and Yu-Ju Oils produced in Formosa. Monopoly Bureau, Government of Formosa. Taihoku 1914. This brochure of about 50 pages is provided with numerous illustrations of Shô-Gyū and of the Yu-Ju-tree, also with many maps showing the distribution of these trees in different parts of Formosa.

acetylation 46.6 to 129.4; soluble in 1 to 12.5 vol. of 80 p.c. alcohol. Of its constituents the following were identified: —

Formaldehyde was identified by the Rimini reaction[1]).

Sabinene. This hydrocarbon was contained in fraction 163 to 167° and was characterized by its oxidation to sabinenic acid (m.p. 57°) and the conversion of the latter into sabina ketone. An attempt to identify *α*-pinene and camphene was unsuccessful. At least no nitrosochloride and no solid *iso*borneol could be obtained.

Dipentene. From fraction 174 to 178° Nagai obtained dipentene tetrabromide melting at 123 to 124°.

Both *α*- and *γ-terpinene* occur in shô-gyū oil. They were characterized respectively by oxidation to the erythritol (*γ*-terpinene) melting at 236°, and *i*-*α*,*α*'-dihydroxy-*α*-methyl-*α*'-*iso*propyl adipinic acid (*α*-terpinene) melting at 188 to 189°.

The presence of linalool could not be proven satisfactorily.

Fraction 207 to 213° contained *terpinenol*-4 which was identified by converting it into terpinene terpin and 1, 2, 4-trihydroxy terpane. Oxidation with alkaline permanganate converted the trihydroxy terpane into *α*,*α*'-dihydroxy-*α*-methyl-*α*'-*iso*propyl-adipinic acid. This in turn, when oxidized in acid solution with potassium permanganate, yielded *ω*-dimethyl acetonyl acetone. Furthermore, the trihydroxy terpane, when boiled with dilute hydrochloric acid, yielded *p*-cymene and carvenone. The nitrosochloride of the terpinenol-4 melted at 111 to 112°, the nitrolpiperidide at 172 to 174°, the phenyl urethane at 71 to 72°, and the naphthyl urethane at 105.5 to 106.5°. The terpinenol is present in considerable quantity in the oil.

The attempts to prove the presence of camphor and terpineol remained without positive results. On the other hand it was possible to establish the presence of *geraniol*. This alcohol is contained in fraction 97 to 112° (8 mm.). Its diphenyl urethane melted at 80.5°.

Citronellol also occurs in the oil. The silver salt of the acid phthalate melted at 125 to 126°.

Safrol was characterized by its oxidation to piperonylic acid (m. p. 228°), and *eugenol* by its benzoyl ester prepared according to Schotten-Baumann (m. p. 69°). Cadinene (color reaction) may also be present.

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[1]) Comp. Chem. Zentralbl. 1898, I. 1152.

YU-JU OIL.

Nagai described yu-ju oil, as a product having great resemblance to camphor oil. It differs from the latter, however, in not separating solid camphor. The yu-ju tree resembles the camphor tree so closely that it can be distinguished only by the odor of its wood. Genus and species are not known. The tree occurs in the southern part of Formosa where it is known as "oil tree". The natives call it *jû-chiu*, which means oil tree. An annual production of 50 000 to 60 000 kin would easily be possible. The yu-ju oil has the same physical properties as camphor oil, but its optical rotation is lower, $d_{18°}$ 0.942 to $d_{16°}$ 0.972; $\alpha_D + 18.88$ to $+ 29.85°$; $n_{D19°}$ 1.47457 to $n_{D20°}$ 1.47869. It contains the following constituents: *furfuro* (color reaction with anilin hydrochloride and *p*-toluidine acetate) d-*α-pinene* (m. p. of nitrosochloride 107 to 108°; m. p. of nitrol-piperidide 117 to 118°; m. p. of nitrosopinene 131 to 132°) *camphene* (conversion into *iso*borneol melting at 209°; m. p. of phenylurethane 138°), *β-pinene* (m. p. of nopinic acid 126 to 127°), *cineol* (m. p. of cineol-iodol 112°), *dipentene* (m. p. of tetrabromide 124 to 125°), *α-terpineol* (m. p. of nitrosochloride 113°; m. p. of nitrolanilide 155 to 156°; m. p. of phenyl urethane 113°), *safrol* (b. p. 233°; $d_{16°}$ 1.106), *eugenol* (m. p. of benzoyl eugenol 69°) and *camphor* which separated from fraction 110 to 112° (17 mm.) as such. The principal constituent of the oil is cineol.

947. Oil of Yama-nikkei Bark.

From wild cinnamon bark, the Japanese *yama-nikkei* bark (family *Lauraceæ*), Schimmel & Co.[1]) obtained a volatile oil with the following constants: $d_{15°}$ 0.9245; $\alpha_D + 8°34'$; $n_{D20°}$ 1.47779; A.V. 0.6; E.V. 14.8. Soluble in 1 and more vol. of 80 p.c. alcohol. The yield amounted to 1.77 to 2.1 p.c.

The light yellow oil has a strong odor of camphor, reminding at the same time of ginger. The greater portion of the oil distills between 75 and 95 (6 mm.) and congeals in the cold to a magma of *camphor*. Separated by force filter and purified by sublimation it melted at 175°. With semicarbazide it yielded a semicarbazone melting at 236°, the 25 p.c. chloroformic

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[1]) Report of Schimmel & Co. April 1915, 54.

solution of which showed a slight optical rotation, $-0°10'$, in a 20 mm. tube. Judging by the odor, fraction 40 to 75° (6 mm.) appears to contain terpenes and cymene.

948. Parthenoxylon Oil.

In Buitenzorg[1]) there was distilled from the leaves of an unknown Borneo species of *Parthenoxylon (Lauraceæ)* a volatile oil with the following properties: $d_{26°}$ 0.893; $\alpha_D - 17°4'$. The oil contained *cineol* (m. p. of cineol-iodol 110°).

949. Oil of Sachguise.

Sachguise is a resin which, like mastic, is chewed after meals by some inhabitants of the Caucasus. In this manner they cleanse and disinfect their teeth, in part mechanically in part chemically. The resin that was distilled by L. Tschugaeff and J. Surenjanz[2]) was a yellow, fragrant substance obtained from Tiflis where it is sold at 50 cents per kilo.

Distillation with steam yielded 8 p.c. of volatile oil; $d_{16°}$ 0.909; $[\alpha]_D + 36.4°$. The bulk of the oil distilled between 154 and 158° and consisted for the most part of d-α-*pinene* (m. p. of hydrochloride 125°; m. p. of nitrosochloride 103°).

950. Oil of Haitian Sandalwood.

From sandalwood obtained from Port au Prince Roure-Bertrand Fils[3]) obtained 3.8 p.c. of oil which was very viscid, and also in its other properties greatly differed from ordinary sandalwood oil: $d_{15°}$ 0.9799; $\alpha_D + 47°4'$, ester content computed as $CH_3COOC_{15}H_{23}$, 0.4 p.c.; total alcohol content, computed as $C_{15}H_{24}O$, 44.1 p.c.; soluble in 3 vol. and more of 70 p.c. alcohol. Roure-Bertrand Fils promised further communications concerning the sesquiterpene alcohol, also concerning the botanical origin of the wood which is whiter, but less hard, than East Indian sandalwood.

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[1]) Jaarb. dep. Landb. in Ned.-Indië, Batavia 1911, 48.

[2]) Journ. Russ. phys. chem. Soc. 39 (1907), 1324; Chem. Zentralbl. 1908, I. 1180.

[3]) Berichte von Roure-Bertrand Fils October 1907, 15.

Supplement.

Family: UMBELLIFERÆ.

ad 733. Oil of Masterwort[1]).

The oil of *Imperatoria* has recently been examined by F. Lange[2]). It had been obtained from dry Tirolese roots collected from two year old plants with a yield of 1 p.c. and possessed the following properties: $d_{20°}$ 0.8627; $\alpha_{D20} + 59.30°$; A. V. 0.8; S. V. 17.9; E. V. after acetylation .28.34. In addition to free *palmitic acid*, the oil contained the following acids as esters: iso*butyric acid*, iso*valeric acid*, iso*propylidene acetic acid* (ß,ß-dimethyl acrylic acid), *formic acid* and *acetic acid*. Whether the *iso*propylidene acetic acid was originally contained in the plant or resulted from the distillation is still a question.

95 p.c. of the oil consisted of terpenes. Of these *dipentene* (m. p. of dihydrochloride 50°), d-*limonene* (m. p. of nitrolbenzylamine 92 to 93°), α-*pinene* (m. p. nitrolbenzylamine 122 to 123°), and d-*phellandrene* (m. p. of rite 103 to 104°) have been identified. In addition the oil contained an alcohol $C_{10}H_{20}O$ (?) the phenyl urethane of which melted at 145 to 146°. Finally, Lange showed the presence in the oil of a *sesquiterpene*, the dihydrochloride of which melted at 157 to 157.5°.

The angelica aldehyde, stated by Wagner to be a constituent of the oil, could not be found by Lange.

Family: ASCLEPIADACEÆ.

951. Oil of Condurango Bark.

In an exhaustive research of the chemistry of condurango bark (from *Marsdenia Condurango*, Reichenbach fil., family *Asclepiadaceæ*) K. Kubler[3]) describes a volatile which he obtained with a yield of 0.3 p.c. by steam distillation of the

[1]) See p. 373.
[2]) Arbeiten aus dem pharm. Inst. der Univers. Berlin 8 (1911), 98.
[3]) Arch. der Pharm. 246 (1908), 658.

ethereal extract. This was yellow, of an intense but not unpleasant, aromatic, somewhat penetrating odor; b. p. 140° (?); $d_{18°}$ 0.9741; $[\alpha]_D + 6.724°$. Treatment with 3 p.c. sodium hydroxide solution yielded, on the one hand, a neutral portion with an agreeably aromatic odor (b. p. 225°; d 0.927; $[\alpha]_D + 19.56°$), and an acid portion which crystallized and consisted of a mixture of higher fatty acids.

Family: VERBENACEÆ.

952. Oil of Lippia scaberrima.

Lippia scaberrima, Sonder occurs in Orange River Colony, South Africa, where it is popularly known as *Beukess boss.* In a thorough chemical examination by F. B. Power and F. Tutin[1]) of the plant the oil was also obtained.

The alcoholic extract of the plant, the odor of which reminded of lavender and sage, was distilled with steam. The oil obtained amounted to 0.25 p.c. with reference to the dry plant. It was yellowish-brown and its odor was similar to that of the plant and distinctly camphoraceous. B. p. 220 to 230°; $d_{15°}$ 0.9500; $\alpha_D + 7°36'$; readily soluble in 50 p.c. alcohol. With ferric chloride it yields a light brown color. In the aqueous distillate the presence of *formic* and *butyric acids,* in small quantities, could be shown.

[1]) Arch. der Pharm. 245 (1907), 337; Americ. Journ. Pharm. 79 (1907), 449.

Errata.

Page 242, 8th line from above, to add:
From the bark of this kind the authors obtained a red oil ($d_{15°}$ 0.898), which contained neither phellandrene nor cineol.

Page 14, 18th line from below, to read: *Garelli* instead of Carelli.
Page 167, 4th line from above, to read: *Sakais* instead of Sokais.
Page 487, 5th line from below, to read: $C_{10}H_{16}O_2$ instead of $C_{11}H_{16}O_2$.
Page 609, 1st line from above, to read: *Sprinz* instead of Spring.

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